Reliable Nonlinear Parameter Estimation in VLE Modeling

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Abstract

The reliable solution of nonlinear parameter estimation problems is an important computational problem in the modeling of vapor-liquid equilibrium (VLE). Conventional solution methods may not be reliable since they do not guarantee convergence to the global optimum sought in the parameter estimation problem. We demonstrate here a technique, based on interval analysis, that can solve the nonlinear parameter estimation problem with complete reliability, providing a mathematical and computational guarantee that the global optimum is found. As an example, we consider the estimation of parameters in the Wilson equation, using VLE data sets from a variety of binary systems. Results indicate that several sets of parameter values published in the DECHEMA VLE Data Collection correspond to local optima only, with new globally optimal parameter values found by using the interval approach. When applied to VLE modeling, the globally optimal parameters can provide significant improvements in predictive capability. For example, in one case, when the previously published locally optimal parameters are used, the Wilson equation does not predict experimentally observed homogeneous azeotropes, but, when the globally optimal parameters are used, the azeotropes are predicted.

1 Introduction

Parameter estimation is a common problem in many areas of science and engineering, including such applications as the modeling of reaction kinetics and phase equilibrium. The goal is to determine values of model parameters that provide the best fit to measured data, generally based on some type of least squares or maximum likelihood criterion. This may require the solution of a nonlinear and frequently nonconvex optimization problem, which often may be formulated either in constrained or unconstrained form.

Many different local methods have been proposed to efficiently perform the constrained or unconstrained optimization. Many of these local optimization techniques use gradient-based approaches; these include Gauss-Newton methods (e.g., [1–4]), Gauss-Marquardt methods (e.g., [5]), and successive quadratic programming (SQP) methods (e.g., [6,7]). Alternatively, if gradient evaluations are expensive or there are difficulties with singularities, then non-gradient methods, such as the simplex pattern search may be used (e.g., [8,9]).

It is not uncommon for the objective function in nonlinear parameter estimation problems to be nonconvex and thus to potentially have multiple local optima. However, the standard methods, such as those mentioned above, used to solve these problems are local methods that provide no guarantee that the global optimum, and thus the best set of model parameters, has been found. Therefore, there is a need for global optimization in nonlinear parameter estimation. One approach that has been suggested is adaptive random search (e.g., [10,11]). Here the search for the optimal parameter values has a randomized component, allowing the potential for discovering multiple local optima. However, such stochastic methods cannot provide any mathematical guarantees that the global optimum has been found. Another approach, suggested by Esposito and Floudas [12,13], is to reformulate the problem in terms of convex underestimating functions and then use a branch and bound procedure. This is a deterministic global optimization method that can

provide a theoretical guarantee of global optimality. One difficulty with this approach is that in general it is necessary to perform problem reformulations and develop convex underestimators specific to each new application. Also, branch and bound methods implemented in floating point arithmetic may be vulnerable to rounding error problems, and thus lose their theoretical guarantees. An alternative approach for global optimization in this context is the use of interval analysis. For example, Moore et al. [14] and Csendes and Ratz [15] have both used parameter estimation as an example in demonstrating more general algorithms based on interval methods.

We demonstrate here the use of interval analysis for determining a global optimum in nonlinear parameter estimation problems of interest in modeling VLE. It is shown that even for relatively simple models, such as the Wilson equation, multiple local optima can occur in parameter estimation. It is also shown that, for some data sets, parameter values published in the DECHEMA VLE Data Collection [8] correspond to a local but not global optimum. We then demonstrate how a global optimization procedure based on interval analysis can be used to reliably determine the globally optimal parameter values. The method used involves the use of an interval Newton technique combined with interval branch and bound. This method provides a mathematical *and* computational guarantee of global optimality in parameter estimation. The reliability of the method is demonstrated using several VLE data sets, with the globally optimal parameters compared to published values [8] obtained by using local methods. The effect of using the globally, as opposed to locally, optimal parameter values in VLE calculations is also considered.

2   Parameter Estimation

Several good introductions to the problem of parameter estimation are available (e.g, [16–18]). Suppose that observations y_{ji} of $i = 1, \ldots, m$ dependent response variables from $j = 1, \ldots, n$ experiments are

available, and the responses are to be fit to a model taking an explicit form $y_{ji} = f_i(\mathbf{x}_j, \boldsymbol{\theta})$, with independent variables $\mathbf{x}_j = (x_{j1}, x_{j2}, \ldots, x_{jp})^{\mathrm{T}}$ and parameters $\boldsymbol{\theta} = (\theta_1, \theta_2, \ldots, \theta_q)^{\mathrm{T}}$. Measurement errors in $\mathbf{x}_j$ can either be neglected or treated using an error-in-variables approach. Various objective functions (or estimators) $\phi(\boldsymbol{\theta})$ can be used to determine the parameter values that provide the "best" fit. In many circumstances, a maximum likelihood criterion is most appropriate. However, if a diagonal covariance matrix is assumed, with systematic measurement errors accounted for by taking the diagonal elements to be proportional to the square of the measurements y_{ji}, this can be simplified to the widely used relative least squares criterion,

$$\min_{\boldsymbol{\theta}} \phi(\boldsymbol{\theta}) \equiv \sum_{j=1}^{n} \sum_{i=1}^{m} \left(\frac{y_{ji} - f_i(\mathbf{x}_j, \boldsymbol{\theta})}{y_{ji}} \right)^2. \tag{1}$$

Since the relative least squares estimator is the objective function used by Gmehling et al. [8], and we intend to make comparisons to the parameter values reported there, this is the objective function that will be used here as well. The minimization of $\phi(\boldsymbol{\theta})$ can be treated either as a constrained, or, by substitution of the model into the objective function, unconstrained minimization problem. We will consider only the unconstrained formulation here. For minimizing $\phi(\boldsymbol{\theta})$, a wide variety of standard minimization techniques are available. However, in general, these are local methods that provide no certainty that a global minimum has been found. A technique is needed that can find the global minimum of $\phi(\boldsymbol{\theta})$ with mathematical and computational certainty. Interval analysis provides such a technique. While we concentrate here on interval methods for solving the unconstrained optimization problem, interval analysis can be used for the solution of constrained problems as well [19-20].

3 Interval Analysis

A real interval Z is defined as the set of real numbers lying between (and including) given upper and lower bounds; i.e., $Z = [z^{\mathrm{L}}, z^{\mathrm{U}}] = \{z \in \Re \mid z^{\mathrm{L}} \le z \le z^{\mathrm{U}}\}$. A real interval vector $\mathbf{Z} = (Z_1, Z_2, \ldots, Z_n)^{\mathrm{T}}$

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has n real interval components and can be interpreted geometrically as an n-dimensional rectangle. Note that in this section lower case quantities are real numbers and upper case quantities are intervals. Several good introductions to interval analysis are available (e.g., [19-21]).

Of particular interest here is the interval Newton technique. Given a nonlinear equation system with a finite number of real roots in some initial interval, this technique provides the capability to find (or, more precisely, narrowly enclose) all the roots of the system within the given initial interval. For the unconstrained minimization of the relative least squares function $\phi(\boldsymbol{\theta})$, a common approach is to use the gradient of $\phi(\boldsymbol{\theta})$ and seek a solution of $\mathbf{g}(\boldsymbol{\theta}) \equiv \nabla\phi(\boldsymbol{\theta}) = \mathbf{0}$; that is, to seek a stationary point of $\phi(\boldsymbol{\theta})$. The global minimum will be a root of this nonlinear equation system, but there may be many other roots as well, representing local minima and maxima and saddle points. Thus, for this approach to be reliable, the capability to find all the roots of $\mathbf{g}(\boldsymbol{\theta}) = \mathbf{0}$ is needed, and this is provided by the interval Newton technique. In practice, the interval Newton procedure can also be combined with an interval branch and bound technique, so that roots of $\mathbf{g}(\boldsymbol{\theta}) = \mathbf{0}$ that cannot be the global minimum need not be found. The solution algorithm is applied to a sequence of intervals, beginning with some initial interval $\Theta^{(0)}$ specified by the user. This initial interval can be chosen to be sufficiently large to enclose all physically feasible behavior. The solution algorithm is, of course, only guaranteed to converge to a global solution that is a stationary point within the initial interval $\Theta^{(0)}$ chosen for the parameters. The procedure used to establish initial parameter bounds in this study is described below in Section 4.

For an interval $\Theta^{(k)}$ in the sequence, the first step in the solution algorithm is the *function range test*. Here an *interval extension* $\mathbf{G}(\Theta^{(k)})$ of the function $\mathbf{g}(\boldsymbol{\theta})$ is calculated. An interval extension provides upper and lower bounds on the range of values that a function may have in a given interval. It is often computed by substituting the given interval into the function and then evaluating the function using interval arithmetic. The interval extension so determined is often wider than the actual range of function values, but it always

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includes the actual range. If there is any component of the interval extension $\mathbf{G}(\boldsymbol{\Theta}^{(k)})$ that does not contain zero, then we may discard the current interval $\boldsymbol{\Theta}^{(k)}$, since the range of the function does not include zero anywhere in this interval, and thus no solution of $\mathbf{g}(\boldsymbol{\theta}) = \mathbf{0}$ exists in this interval. We may then proceed to consider the next interval in the sequence, since the current interval cannot contain a stationary point of $\phi(\boldsymbol{\theta})$. Otherwise, if $\mathbf{0} \in \mathbf{G}(\boldsymbol{\Theta}^{(k)})$, then testing of $\boldsymbol{\Theta}^{(k)}$ continues.

The next step is the *objective range test*. The interval extension $\Phi(\boldsymbol{\Theta}^{(k)})$, which contains the range of $\phi(\boldsymbol{\theta})$ over $\boldsymbol{\Theta}^{(k)}$, is computed. If the lower bound of $\Phi(\boldsymbol{\Theta}^{(k)})$ is greater than a known upper bound on the global minimum of $\phi(\boldsymbol{\theta})$, then $\boldsymbol{\Theta}^{(k)}$ cannot contain the global minimum and need not be further tested. Otherwise, testing of $\boldsymbol{\Theta}^{(k)}$ continues. The upper bound on the global minimum of $\phi(\boldsymbol{\theta})$ used for comparison in this step can be determined and updated in a number of different ways. Here we simply use the upper bounds of previously tested $\boldsymbol{\Theta}$ intervals that may contain stationary points. An approach that is usually more efficient, though requires additional objective function evaluations, is to use point evaluations of $\phi(\boldsymbol{\theta})$ done at the midpoint of previously tested $\boldsymbol{\Theta}$ intervals that may contain stationary points. We have used this procedure in solving larger parameter estimation problems than described here (see Section 6).

The next step is the interval Newton test. Here the linear interval equation system

$$G'(\boldsymbol{\Theta}^{(k)})(\mathbf{N}^{(k)} - \boldsymbol{\theta}^{(k)}) = -\mathbf{g}(\boldsymbol{\theta}^{(k)}) \tag{2}$$

is set up and solved for a new interval $\mathbf{N}^{(k)}$, where $G'(\boldsymbol{\Theta}^{(k)})$ is an interval extension of the Jacobian of $\mathbf{g}(\boldsymbol{\theta})$, i.e., the Hessian of $\phi(\boldsymbol{\theta})$, over the current interval $\boldsymbol{\Theta}^{(k)}$, and $\boldsymbol{\theta}^{(k)}$ is a point in the interior of $\boldsymbol{\Theta}^{(k)}$, usually taken to be the midpoint. It has been shown (e.g., [19–21]) that any root $\boldsymbol{\theta}^* \in \boldsymbol{\Theta}^{(k)}$ is also contained in the *image* $\mathbf{N}^{(k)}$, implying that if there is no intersection between $\boldsymbol{\Theta}^{(k)}$ and $\mathbf{N}^{(k)}$ then no root exists in $\boldsymbol{\Theta}^{(k)}$, and suggesting the iteration scheme $\boldsymbol{\Theta}^{(k+1)} = \boldsymbol{\Theta}^{(k)} \cap \mathbf{N}^{(k)}$. In addition to this iteration step, which can be used to tightly enclose a solution, it has been proven (e.g., [19–21]) that if $\mathbf{N}^{(k)}$ is contained completely

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within $\Theta^{(k)}$, then there is *one and only one root* contained within the current interval $\Theta^{(k)}$. This property is quite powerful, as it provides a mathematical guarantee of the existence and uniqueness of a root within an interval when it is satisfied.

There are thus three possible outcomes to the interval Newton test, as shown schematically for a two variable problem in Figures 1–3. The first possible outcome (Figure 1) is that $\mathbf{N}^{(k)} \subset \Theta^{(k)}$. This represents mathematical proof that there exists a *unique* solution to $\mathbf{g}(\boldsymbol{\theta}) = \mathbf{0}$ within the current interval $\Theta^{(k)}$, and that that solution also lies within the image $\mathbf{N}^{(k)}$. This solution can be rigorously enclosed, with quadratic convergence, by applying the interval Newton step to the image and repeating a small number of times, until the relative diameter of the interval containing this solution is less than a specified tolerance (typically about 10^{-10}). Alternatively, convergence to a point approximation of the solution can be guaranteed using a routine point Newton method starting from anywhere inside of the current interval. The next interval in the sequence can now be tested, beginning with the function range test. The second possible outcome (Figure 2) is that $\mathbf{N}^{(k)} \cap \Theta^{(k)} = \emptyset$. This provides mathematical proof that no solutions of $\mathbf{g}(\boldsymbol{\theta}) = \mathbf{0}$ exist within the current interval. Thus, the current interval can be discarded and testing of next interval can begin. The final possible outcome (Figure 3) is that the image $\mathbf{N}^{(k)}$ lies partially within the current interval $\Theta^{(k)}$. In this case, no conclusions can be made about the number of solutions in the current interval. However, it is known that any solutions that do exist must lie in the intersection $\Theta^{(k)} \cap \mathbf{N}^{(k)}$. If the intersection is sufficiently smaller than the current interval, one can proceed by reapplying the interval Newton test to the intersection. Otherwise, the intersection is bisected, and the resulting two intervals added to the sequence of intervals to be tested. This approach is referred to as an interval-Newton/generalized-bisection (IN/GB) method.

Implementing the series of tests outlined above, we can proceed until all regions which cannot contain the global minimum are eliminated. In the example problems considered below, we are frequently interested in finding not only the global minimum, but all local minima as well, for purposes of comparison with results

given in Gmehling et al. [8]. In this case, the objective range test described above is turned off, and the result is that enclosures of all stationary points of $\phi(\boldsymbol{\theta})$, i.e. roots of $\mathbf{g}(\boldsymbol{\theta}) = \mathbf{0}$, are found. It should be emphasized that, when machine computations with interval arithmetic operations are done, the endpoints of an interval are computed with a directed outward rounding. That is, the lower endpoint is rounded down to the next machine-representable number and the upper endpoint is rounded up to the next machine-representable number. In this way, through the use of interval, as opposed to floating point arithmetic, any potential rounding error problems are eliminated. Overall, the IN/GB method described above provides an procedure that is mathematically *and* computationally guaranteed to find the global minimum of $\phi(\boldsymbol{\theta})$, or, if desired, to enclose *all* of its stationary points (within, of course, the specified initial parameter interval $\Theta^{(0)}$).

A more detailed description of the interval Newton procedure used here has been given by Schnepper and Stadtherr [22]. Through the addition here of the objective range test, the procedure they describe has been combined with a simple interval branch and bound scheme. Our current implementation of the IN/GB method is based on appropriately modified routines from the packages INTBIS [23] and INTLIB [24]. Additional details concerning the implementation of interval Newton methods, and the theory underlying them, is available from Hansen [19], Kearfott [20] and Neumaier [21].

4   Application to VLE Modeling

Because of its importance in the design of separation systems, much attention has been given to modeling the thermodynamics of phase equilibrium in fluid mixtures. Typically these models take the form of excess Gibbs energy models or equation of state models, with binary parameters in the models determined by parameter estimation from experimental data. The problem of estimating model parameters from experimental VLE data has attracted significant attention (e.g., [2,3,5,11,25–29]), although other types of data,

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such as VLL (e.g., [30]) or ion-exchange equilibrium (e.g., [9]) can also be used.

As an example, we consider here the estimation from binary VLE data of the energy parameters in the Wilson equation for liquid phase activity coefficient. Expressed in terms of the molar excess Gibbs energy g^E for a binary system, and the liquid-phase mole fractions x_1 and x_2, the Wilson equation is

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \tag{3}$$

from which expressions for the activity coefficients are

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \tag{4}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]. \tag{5}$$

The binary parameters Λ_{12} and Λ_{21} are given by

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left[-\frac{\theta_1}{RT} \right] \tag{6}$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left[-\frac{\theta_2}{RT} \right], \tag{7}$$

where v_1 and v_2 are the pure component liquid molar volumes, T is the system temperature and θ_1 and θ_2 are the energy parameters that need to be estimated.

Given VLE measurements and assuming an ideal vapor phase, experimental values $\gamma_{1,\mathrm{exp}}$ and $\gamma_{2,\mathrm{exp}}$ of the activity coefficients can be obtained from the relation

$$\gamma_{i,\mathrm{exp}} = \frac{y_{i,\mathrm{exp}} P_{\mathrm{exp}}}{x_{i,\mathrm{exp}} P_i^0}, \quad i = 1, 2, \tag{8}$$

where P_i^0 is the vapor pressure of pure component i at the system temperature T. For the example problems here we follow Gmehling et al. [8] and use the relative least squares objective

$$\phi(\boldsymbol{\theta}) \equiv \sum_{j=1}^{n} \sum_{i=1}^{2} \left(\frac{\gamma_{ji,\mathrm{exp}} - \gamma_{ji,\mathrm{calc}}(\boldsymbol{\theta})}{\gamma_{ji,\mathrm{exp}}} \right)^2, \tag{9}$$

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where the $\gamma_{ji,\text{calc}}(\boldsymbol{\theta})$ are calculated from the Wilson equation at conditions (temperature, pressure and composition) coincident to those used when measuring $\gamma_{ji,\text{exp}}$. This parameter estimation problem has been solved for a large number of systems, and results presented in the DECHEMA VLE Data Collection [8], along with the raw VLE data.

In order to apply the interval method described above, a reasonable initial interval $\Theta^{(0)} = [\Theta_1^{(0)}, \Theta_2^{(0)}]^T$ for the Wilson energy parameters θ_1 and θ_2 needs to be determined. One approach to doing this is by considering the range of infinite dilution activity coefficients γ_i^{∞}. According to the Wilson model, the activity coefficients at infinite dilution are given by

$$\ln \gamma_1^{\infty} = 1 - \ln \frac{v_2}{v_1} + \frac{\theta_1}{RT} - \frac{v_1}{v_2} \exp\left(-\frac{\theta_2}{RT}\right) \tag{10}$$

$$\ln \gamma_2^{\infty} = 1 - \ln \frac{v_1}{v_2} + \frac{\theta_2}{RT} - \frac{v_2}{v_1} \exp\left(-\frac{\theta_1}{RT}\right). \tag{11}$$

A survey of infinite dilution activity coefficient data [31,32] for a large number of binary systems indicates that observed data fall in the interval [0.03, 109000]. If the other quantities in Eqs. (10) and (11) are given the reasonable enclosures [0.1, 10] for v_2/v_1 and [200, 600] K for T, then the energy parameter range $\Theta_1 = \Theta_2 = [-8119, 123419]$ cal/mol can be computed. To provide for a substantial margin of safety in the example problems, this estimated range for the parameters is extended to $\Theta_1^{(0)} = \Theta_2^{(0)} = [-8500, 320000]$ cal/mol. This is the initial interval used in the studies reported below. Since this is a very wide interval based on physical considerations, we believe that it is extremely likely that it will contain the globally optimal parameter values. However, it should be emphasized again that the solution algorithm is, of course, only guaranteed to converge to a global solution that is a stationary point within this chosen initial parameter interval. It should also be noted that other approaches, including the use of system-specific information, could be used to establish reasonable initial bounds.

As one of the most frequently used and cited data collections in chemical engineering, the DECHEMA

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VLE Data Collection [8] gives both raw VLE data and parameter estimation results for θ_1 and θ_2 based on the relative least squares objective. Since Gmehling et al. [8] used a local simplex pattern search technique [33] for minimizing $\phi(\boldsymbol{\theta})$ in the parameter estimation problem, it is possible that the reported values of θ_1 and θ_2 do not correspond to a global minimum in $\phi(\boldsymbol{\theta})$. In some systems, the parameter values determined from different data sets are highly inconsistent, suggesting the possibility of multiple local minima in $\phi(\boldsymbol{\theta})$. To investigate this, for several binary systems, we selected isothermal and/or isobaric data sets, with at least eight data points, and re-solved these parameter estimation problems for the global minimum using the interval method suggested here.

5 Results

5.1 Problem 1

As the first example we consider the binary system water(1) – formic acid(2), using 24 VLE data sets at various isobaric conditions from the DECHEMA VLE Data Collection. In Table 1, each data set is identified by its volume and page number in DECHEMA. The association of formic acid in the vapor phase was accounted for using the same procedure as shown in DECHEMA.

The results for θ_1 and θ_2 and $\phi(\boldsymbol{\theta})$ from DECHEMA and from the interval method (IN/GB) suggested here are summarized in Table 1, along with the number of local minima found for each problem. For purposes of determining all stationary local minima, the objective range test was turned off, as explained above. It should be noted that, while point approximations are reported here for the IN/GB results, we have actually determined verified enclosures of each stationary point and computed $\phi(\boldsymbol{\theta})$ for this enclosure. Each such enclosure is known to contain a *unique* root, based on the interval-Newton uniqueness test described above. Thus, for example, for data set 2 in Table 1, the actual results of IN/GB are

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$\theta_1 \in [25082.9286669347, 25082.9286670875]$, $\theta_2 \in [-1336.49711840838, -1336.49711840836]$, and $\phi(\boldsymbol{\theta}) \in [0.0814284045014626, 0.0814284045015501]$. Similarly narrow enclosures were determined in all cases with IN/GB.

New globally optimal results found using IN/GB are shown in bold in Table 1. It can be seen that 22 of the 24 problems have multiple local minima, and that in 12 of these cases (data sets 2–11, 16 and 21) the results presented in DECHEMA are not globally optimal. There are two cases (data sets 2 and 3) that are unusual in that these are the only cases in which the point reported in DECHEMA is *not* a stationary point, and so represents neither a local nor global minimum. If these were stationary points, they would have been found using IN/GB, since the θ_1 and θ_2 values at these points are well within the initial parameter interval $\Theta_1^{(0)} = \Theta_2^{(0)} = [-8500, 320000]$ used. The fact that these are not stationary points was also verified by computing an interval enclosure of the gradient at this point and noting that it does not contain zero. In all the other cases, the simplex pattern search method used in DECHEMA converged to one of the local minima found using the IN/GB approach. In data sets 2 and 3, the pattern search procedure appears to be moving towards the local (and global) minima found using IN/GB, but terminates prematurely. This is likely due to the fact that the objective function is extremely flat in this area, so that premature termination could be caused by rounding errors, or by using too large a convergence tolerance. The improvement in $\phi(\boldsymbol{\theta})$ at the global optimum in comparison to the nonoptimal DECHEMA point is insignificant.

We now look more closely at the results for one data set, namely data set 6. For this case, the interval method (with the objective range test turned off) found five stationary points, including three minima and two saddle points, in the initial interval of interest. These results are summarized in Table 2. The global minimum at $\boldsymbol{\theta} = (-329, 1394)^{\mathrm{T}}$ (root P5) has an objective function value $\phi(\boldsymbol{\theta}) = 0.0819$ that is only about half the magnitude of the local minimum at $\boldsymbol{\theta} = (450, -663)^{\mathrm{T}}$ (root P3) found by Gmehling et al. [8] and reported in the DECHEMA Collection. As is often the case in least squares problems of this sort, all the

minima found lie in a relatively narrow valley in the parameter space.

The performance of the two different parameter sets, corresponding to the local minimum P3 (DECHEMA) and the global minimum P5 (interval method), in predicting the activity coefficients for water and formic acid with the Wilson equation is shown in Figure 4 (water) and Figure 5 (formic acid). It is clear that when the globally optimal parameter values from IN/GB are used in the Wilson equation, it results in less deviation from the experimental values in comparison to the case in which the locally optimal parameters reported in DECHEMA are used.

In determining the global minimum with the interval approach, very wide initial intervals of parameter variables were used, which, as explained above, should be wide enough to enclose any physically feasible solution. The ability to provide a wide initial interval, as opposed to an initial point guess, means that the method is essentially initialization independent. For each data set, the computation time needed to perform the global optimization was roughly from 16 to 50 seconds on a Sun Ultra 2/1300 workstation. The difference in times is due to the differing number of data points in each data set, and the differing number of stationary points found. These computation times are much higher than what is required by the local optimization methods typically used in parameter estimation. Thus, the choice is between fast methods that may give the wrong answer, or slower methods that are guaranteed to give the correct answer.

5.2   Problem 2

The second example is the binary system *tert*-butanol(1) – 1-butanol(2). Six data sets were studied with the results shown in Table 3. In each case, there was a global minimum found by using the interval method (IN/GB) that was substantially different from the local minimum reported in DECHEMA. As an example, data set 6 was used to create relative error plots for the activity coefficients, as shown in Figure 6 (*tert*-butanol) and Figure 7 (1-butanol). As in the previous problem, it can be seen again that the globally optimal

parameter values result in less deviation and provide a better fit to the experimental observations.

5.3 Problem 3

In this example problem and the next one, we will find the globally optimal parameter values, but instead of looking just at the effect on prediction of activity coefficients, as done in the previous examples, we will look at how the improved prediction of activity coefficients affects the prediction of vapor-liquid equilibrium. For this problem, we use one data set for the system water(1) – 1,2-ethanediol(2). As indicated in Table 4, the interval approach (with objective range test turned off) finds two stationary minima, one of which is the local minimum reported in DECHEMA and the other the true global minimum, which has a much smaller objective function value than the local minimum. Figure 8 shows the x-y VLE plots calculated using the globally optimal parameters (IN/GB) and using the locally optimal parameters (DECHEMA), with comparison to the actual experimental data. Clearly the VLE computed using the globally optimal parameters provides a better fit to the experimental data, especially at low water concentrations.

5.4 Problem 4

In this example problem, we look at the effect on prediction of VLE not by using an x-y plot, but by considering the prediction of homogeneous azeotropes. The failure of a model to adequately predict the presence of azeotropes could lead to very serious problems in the design of separation processes. The system used for this problem is benzene(1) – hexafluorobenzene(2), using all ten data sets, both isothermal and isobaric, found in DECHEMA. As shown in Table 5, using the interval method (IN/GB) new globally optimal parameter values are discovered in five of the ten cases. For these five cases, we used both the locally optimal parameters (DECHEMA) and the globally optimal parameters (IN/GB) to predict the presence and location of homogeneous azeotropes. The method of Maier et al. [34], which employs an interval method

and is guaranteed to find all homogeneous azeotropes, or determine with certainty that there are none, was used. Results of the azeotrope calculations are shown in Table 6, along with experimental data [35] indicating that this system has two homogeneous azeotropes. However, when the locally optimal parameters reported in DECHEMA are used in azeotrope prediction, there are three cases in which no azeotrope is found, and in the remaining two cases only one azeotrope is found. Using the globally optimal parameters found using the interval method proposed here, two azeotropes are predicted in all cases. In this case, by finding the globally, as opposed to locally, optimal parameter values, it clearly makes the difference between predicting physical reality or not. While the Wilson equation is capable of predicting the presence of two azeotropes, the predicted location of the azeotropes differs somewhat from the experimental values, especially for the hexafluorobenzene-rich azeotrope. This indicates that the Wilson equation is not an entirely satisfactory model for this system.

While for many of the systems in DECHEMA the parameters reported are in fact globally optimal, the failure of standard local optimization techniques to find the globally optimal parameters is not unique to the above systems, data sets, and model. This can also be observed in other systems in the DECHEMA collection and with models other than the Wilson equation. This should not be surprising, since with traditional local solution techniques, there simply is no guarantee that the global optimum will always be found. Using the interval method described here, such a guarantee can be provided.

6 Concluding Remarks

We have described here a new method for reliably solving nonlinear parameter estimation problems in VLE modeling. The method is based on interval analysis, in particular an interval Newton/generalized bisection algorithm. The approach provides a mathematical and computational guarantee that the global

optimum in the parameter estimation problem is found. We applied the technique here to several systems in which the Wilson activity coefficient model was used. However, the technique is model independent and can be applied in connection with any thermodynamic model for vapor-liquid equilibrium. The approach presented is general purpose and can also be used in connection with other objective functions, such as maximum likelihood, with other types of data, or with other problem formulation, such as error-in-variable. For example, Gau and Stadtherr [36] have recently applied this approach to the solution of an error-in-variables problem [13,37] involving parameter estimation in the van Laar equation. As described by Gau and Stadtherr [36], this problem has 12 variables that must be solved for, which can be done efficiently by using a more efficient approach for updating the upper bound on the global mininum, as noted previously in Section 3, and by using a new type of preconditioner when solving for the interval Newton image.

List of Symbols

f_i, model for dependent variable i.

$\mathbf{g}$, gradient of objective function ϕ.

g^{E}, molar excess Gibbs energy.

$\mathbf{G}$, interval extension of g.

G', interval extension of Hessian of ϕ.

m, number of dependent variables.

n, number of experiments.

$\mathbf{N}$, the interval-Newton image, an interval.

p, number of independent variables.

P, pressure.

P_i^0, vapor pressure of species i.

q, number of parameters.

R, the gas constant.

$\Re$, the set of real numbers.

T, temperature.

v_i, molar volume of species i.

x_i, liquid-phase mole fraction of species i (Section 4).

x_{ji}, i-th independent variable in experiment j (Section 2).

y_i, vapor-phase mole fraction of species i (Section 4).

y_{ji}, i-th dependent variable in experiment j (Section 2).

$Z = [z^{\mathrm{L}}, z^{\mathrm{U}}]$, an interval.

Z, an interval vector.

Greek Letters

γ_i, liquid-phase activity coefficient for species i.

θ_i, i-th parameter.

$\boldsymbol{\theta}$, parameter vector.

$\boldsymbol{\Theta}$, interval parameter vector.

Λ_{ij}, binary parameter in Wilson equation.

ϕ, objective function in parameter estimation.

Subscripts

calc, indicates calculated value.

exp, indicates experimental value.

Superscripts

(k), indicates k-th interval in solution sequence.

∞, indicates infinite dilution.

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Table 1: Parameter estimation for water(1) – formic acid(2) system.

Data Set	Volume: Page[1]	Data points	P (mmHg)	DECHEMA θ_1	DECHEMA θ_2	DECHEMA $\phi(\boldsymbol{\theta})$	IN/GB θ_1	IN/GB θ_2	IN/GB $\phi(\boldsymbol{\theta})$	No. of Minima	CPU time(s)
1	1a:40	8	49	523	-799	0.0197	524	-800	0.0197	3	19.4
2*†	1:11	15	50	8737	-1336	0.0814	**25083**	**-1336**	**0.0814**	2	31.5
3*†	1:28	14	50	8856	-1348	0.1425	**70543**	**-1348**	**0.1425**	2	31.8
4*	1:16	9	70	558	-762	0.0399	**-330**	**1519**	**0.0372**	3	21.4
5*	1:12	16	100	539	-718	0.1650	**-285**	**996**	**0.1114**	3	31.5
6*	1:23	19	100	450	-663	0.1510	**-329**	**1394**	**0.0819**	3	35.2
7*	1a:36	16	100	561	-738	0.1648	**-289**	**1012**	**0.1153**	3	31.6
8*	1:13	14	200	892	-985	0.1410	**-331**	**1250**	**0.0914**	2	25.0
9*	1:17	11	200	370	-608	0.0459	**-340**	**1404**	**0.0342**	3	23.1
10*	1:24	22	200	337	-581	0.3564	**-317**	**981**	**0.3486**	3	50.1
11*	1a:37	14	200	891	-987	0.1302	**-320**	**1218**	**0.0792**	2	24.2
12	1:25	23	400	-317	1146	0.0610	-317	1147	0.0610	3	39.7
13	1:26	25	600	-331	1248	0.0799	-331	1246	0.0799	3	41.2
14	1:14	15	760	-195	759	0.0342	-195	759	0.0342	2	19.1
15	1:15	15	760	-278	1038	0.0106	-278	1038	0.0106	2	16.4
16*	1:18	12	760	-310	1181	0.0151	**2095**	**-1407**	**0.0110**	3	22.6
17	1:20	28	760	-282	985	0.353	-282	984	0.353	2	28.5
18	1:21	12	760	-366	1513	0.0257	-365	1509	0.0257	3	20.6
19	1:22	15	760	1067	-1122	0.0708	1065	-1120	0.0708	2	28.2
20	1:27	27	760	-310	1134	0.0485	-310	1134	0.0485	2	29.5
21*	1:34	14	760	694	-941	0.1606	**-387**	**1755**	**0.1408**	3	25.8
22	1a:38	15	760	-199	771	0.0342	-198	769	0.0342	2	18.9
23	1b:15	17	1471	1381	-1376	0.2619	1380	-1376	0.2619	1	26.9
24	1b:16	12	2237	1469	-1396	0.0885	1467	-1395	0.0883	1	19.7

[1]Refers to volume and page numbers in DECHEMA VLE Data Collection [8].

*New globally optimal parameters found.

†Point from DECHEMA is neither local nor global minimum. See text for discussion. Value of $\phi(\boldsymbol{\theta})$ at the DECHEMA point is greater than the global minimum at the IN/GB point in the fifth significant figure for data set 2 and in the sixth significant figure for data set 3.

Table 2: Stationary Points (Roots) for Data Set 6.

Root	θ_1, θ_2	Eigenvalues of Hessian	$\phi(\boldsymbol{\theta})$	Status
P1	(1958, -1251)	7.55E-5, 2.58E-7	0.164	minimum
P2	(1165, -1083)	6.83E-5, -1.44E-7	0.178	saddle
P3	(452, -664)	6.97E-5, 9.42E-8	0.151	minimum
P4	(-37.8, 38.5)	9.08E-5, -3.54E-7	0.197	saddle
P5	(-329, 1394)	1.23E-4, 1.47E-7	0.0819	global minimum

Table 3: Parameter estimation for tert-butanol(1) – 1-butanol(2) system.

Data Set	Volume: Page[1]	Data points	P (mmHg)	DECHEMA			IN/GB			No. of Minima	CPU time(s)
				θ_1	θ_2	$\phi(\boldsymbol{\theta})$	θ_1	θ_2	$\phi(\boldsymbol{\theta})$		
1*	2b:156	9	100	951	-602	0.0136	**-568**	**745**	**0.0103**	2	16.5
2*	2b:157	9	300	1068	-638	0.0158	**-525**	**626**	**0.0130**	2	14.4
3*	2b:158	9	500	901	-594	0.0097	**-718**	**1265**	**0.0069**	2	16.2
4*	2b:159	9	700	801	-561	0.0174	**-734**	**1318**	**0.0137**	2	16.7
5*	2f:151	17	760	153	-203	0.1300	**-793**	**1757**	**0.1164**	3	20.9
6*	2f:152	14	760	848	-606	0.0333	**-865**	**2420**	**0.0111**	2	14.1

[1]Refers to volume and page numbers in DECHEMA VLE Data Collection [8].
*New globally optimal parameters found.

Table 4: Parameter estimation for water(1) – 1,2-ethanediol(2) system.

Data Set	Volume: Page[1]	Data points	P (mmHg)	DECHEMA			IN/GB			No. of Minima	CPU time(s)
				θ_1	θ_2	$\phi(\boldsymbol{\theta})$	θ_1	θ_2	$\phi(\boldsymbol{\theta})$		
1*	1a:171	18	430	71	-94	3.0515	**5072**	**-1922**	**1.0392**	2	27.4

[1]Refers to volume and page numbers in DECHEMA VLE Data Collection [8].
*New globally optimal parameters found.

Table 5: Parameter estimation for benzene(1) – hexafluorobenzene(2) system.

Data Set	Volume: Page[1]	Data points	$T(^oC)$ or P (mmHg)	DECHEMA			IN/GB			No. of Minima	CPU time(s)
				θ_1	θ_2	$\phi(\boldsymbol{\theta})$	θ_1	θ_2	$\phi(\boldsymbol{\theta})$		
1*	7:228	10	T=30	437	-437	0.0382	**-468**	**1314**	**0.0118**	2	19.2
2*	7:229	10	40	405	-405	0.0327	**-459**	**1227**	**0.0079**	2	17.6
3*	7:230	10	50	374	-374	0.0289	**-449**	**1157**	**0.0058**	2	15.8
4*	7:233	11	50	342	-342	0.0428	**-424**	**984**	**0.0089**	2	14.1
5	7:231	10	60	-439	1096	0.0047	-439	1094	0.0047	2	12.4
6	7:232	9	70	-424	1035	0.0032	-425	1036	0.0032	2	10.1
7*	7:234	17	P=300	344	-347	0.0566	**-432**	**993**	**0.0149**	2	22.5
8	7:235	16	500	-405	906	0.0083	-407	912	0.0083	2	18.3
9	7:236	17	760	-407	923	0.0057	-399	908	0.0053	1	17.9
10	7:226	29	760	-333	702	0.0146	-335	705	0.0146	2	26.1

[1]Refers to volume and page numbers in DECHEMA VLE Data Collection [8].
*New globally optimal parameters found.

Table 6: Azeotrope prediction for benzene(1) – hexafluorobenzene(2)system.

Data Set	$T(^oC)\,or$ P (mmHg)	DECHEMA			IN/GB			Experiment		
		x_1	x_2	P or T	x_1	x_2	P or T	x_1	x_2	P or T
1	T=30	0.0660	0.9340	P=107	0.0541	0.9459	P=107	0.15	0.85	P=107
					0.9342	0.0658	121	0.95	0.05	120
2	40	0.0315	0.9685	168	0.0761	0.9239	168	0.16	0.84	167
					0.9244	0.0756	185	0.93	0.07	183
3	50	NONE			0.0988	0.9012	255	0.17	0.83	254
					0.9114	0.0886	275	0.90	0.10	273
4	50	NONE			0.0588	0.9412	256	0.17	0.83	254
					0.9113	0.0887	274	0.90	0.10	273
7	P=300	NONE			0.1612	0.8388	T=54.13	0.20	0.80	T=54.55
					0.9315	0.0685	52.49	0.89	0.11	52.50

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Figure Captions

Figure 1. The computed image $\mathbf{N}^{(k)}$ is a subset of the current interval $\Theta^{(k)}$. This is mathematical proof that there is a unique solution of the equation system in the current interval, and furthermore that this unique solution is also in the image.

Figure 2. The computed image $\mathbf{N}^{(k)}$ has a null intersection with the current interval $\Theta^{(k)}$. This is mathematical proof that there is no solution of the equation system in the current interval.

Figure 3. The computed image $\mathbf{N}^{(k)}$ has a nonnull intersection with the current interval $\Theta^{(k)}$. Any solutions of the equation system must lie in the intersection of the image and the current interval.

Figure 4. The relative error in Problem 1 (data set 6) between calculated and experimental activity coefficients for water resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB. The relative error for a data point at $x_1 = 0.0802$ is off scale (roughly at -0.22) for both cases.

Figure 5. The relative error in Problem 1 (data set 6) between calculated and experimental activity coefficients for formic acid resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB.

Figure 6. The relative error in Problem 2 (data set 6) between calculated and experimental activity coefficients for *tert*-butanol resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB.

Figure 7. The relative error in Problem 2 (data set 6) between calculated and experimental activity coefficients for 1-butanol resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB.

Figure 8. Comparison of VLE prediction for water(1) – 1,2-ethanedial(2) in Problem 3 resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB.
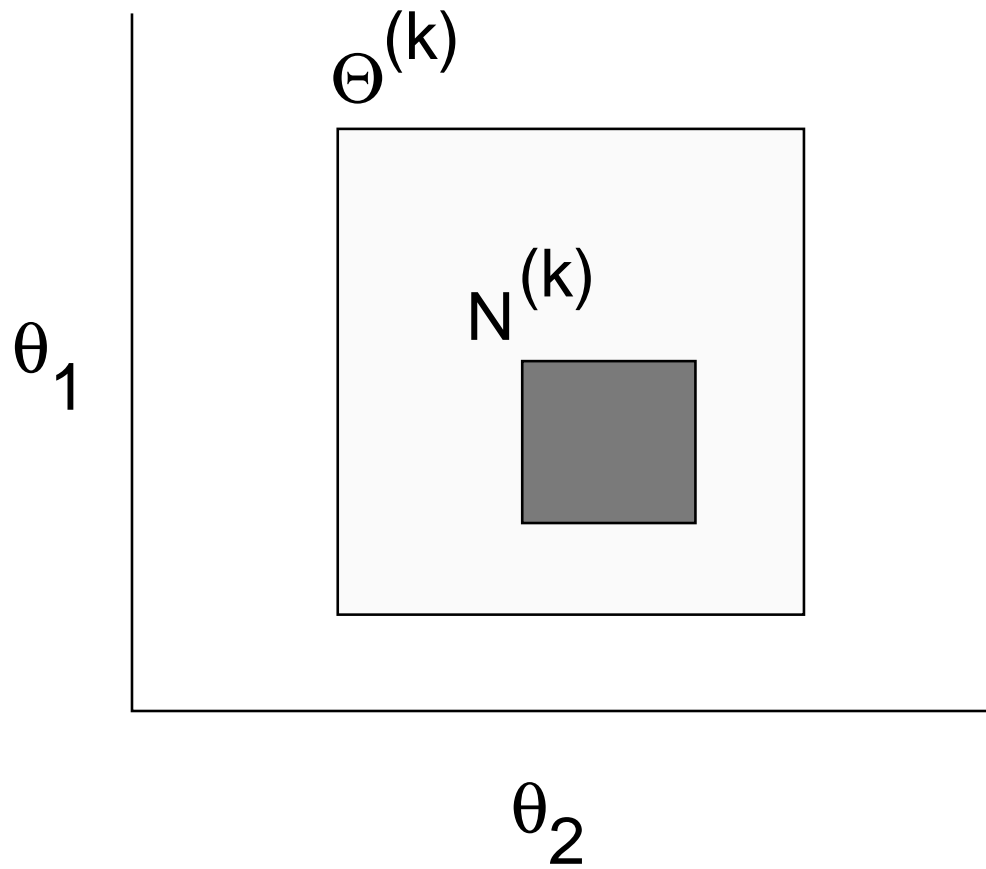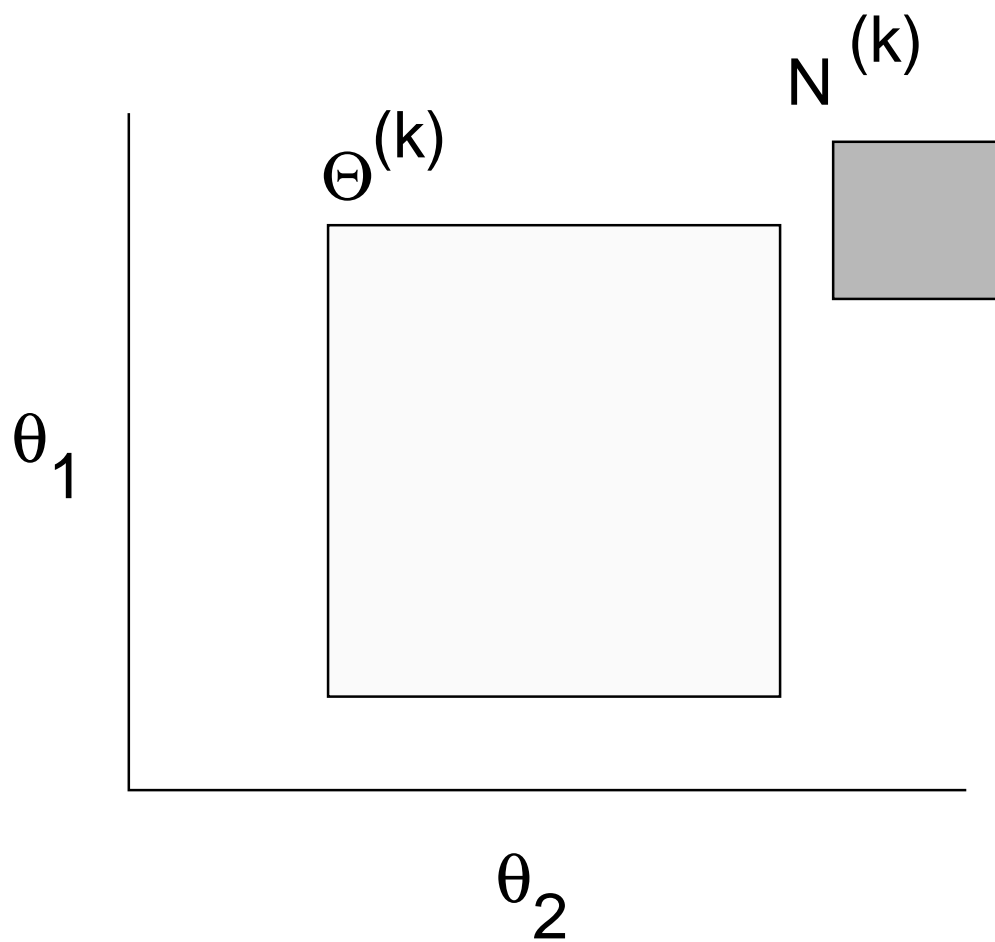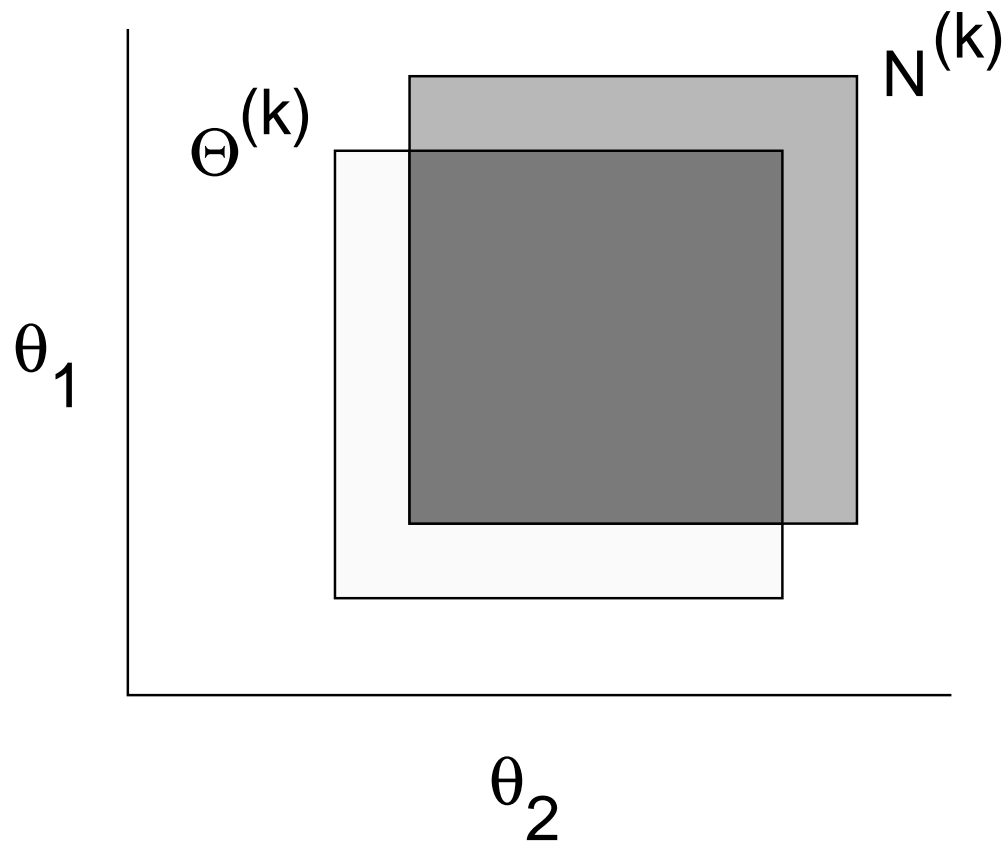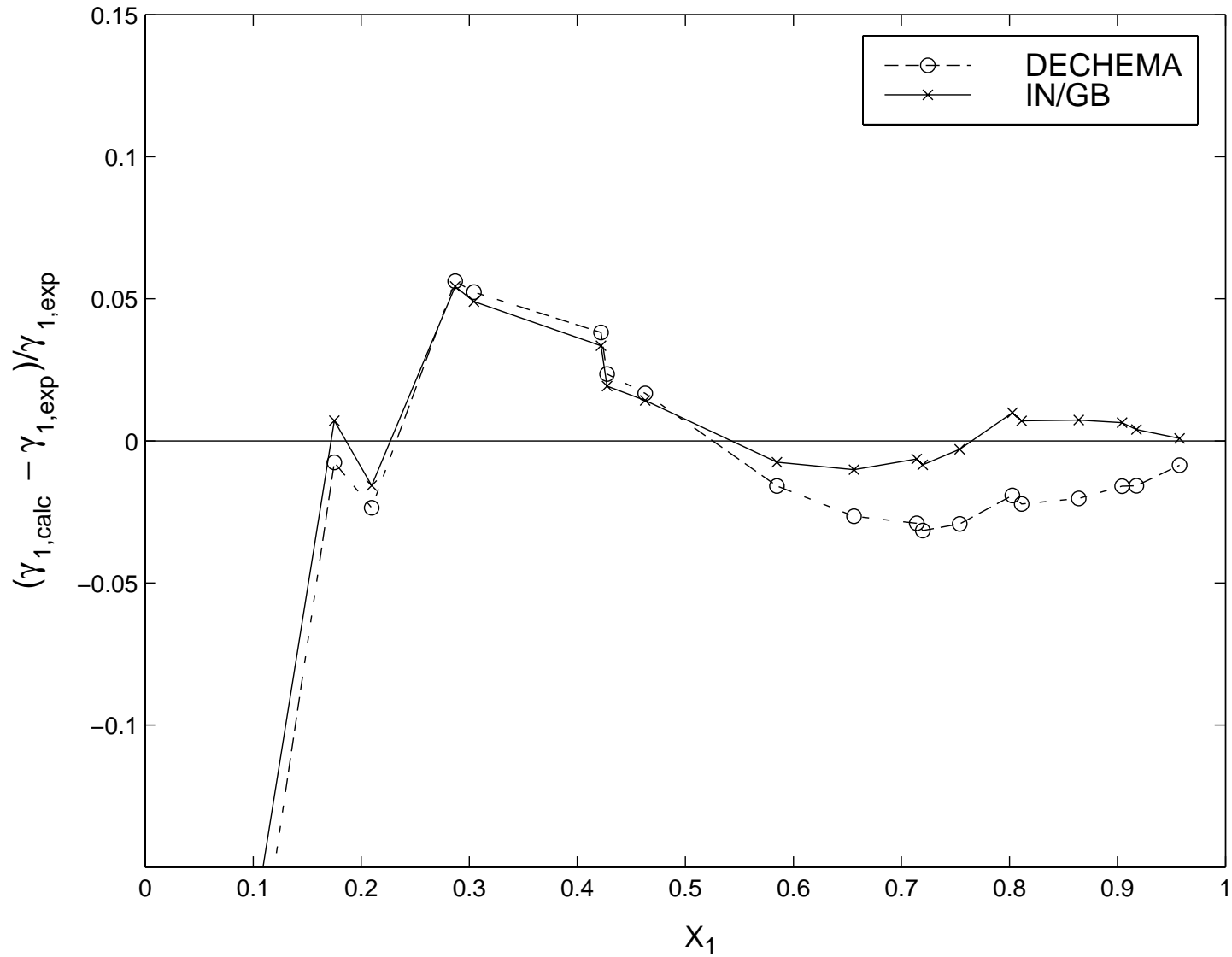
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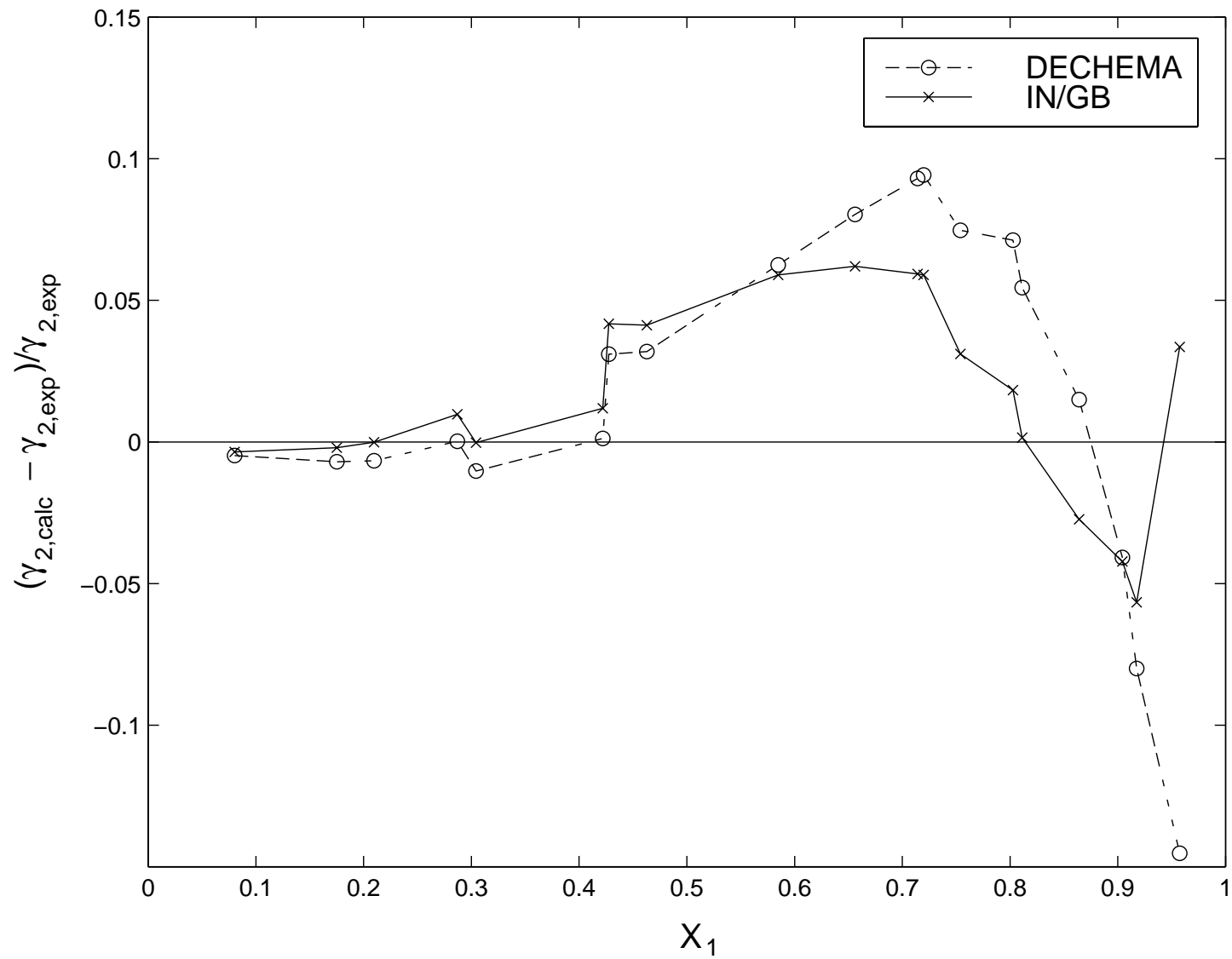
Figure 4: The relative error in Problem 1 (data set 6) between calculated and experimental activity coefficients for water resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB. The relative error for a data point at $x_1 = 0.0802$ is off scale (roughly at -0.22) for both cases.

Figure 5: The relative error in Problem 1 (data set 6) between calculated and experimental activity coefficients for formic acid resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB.
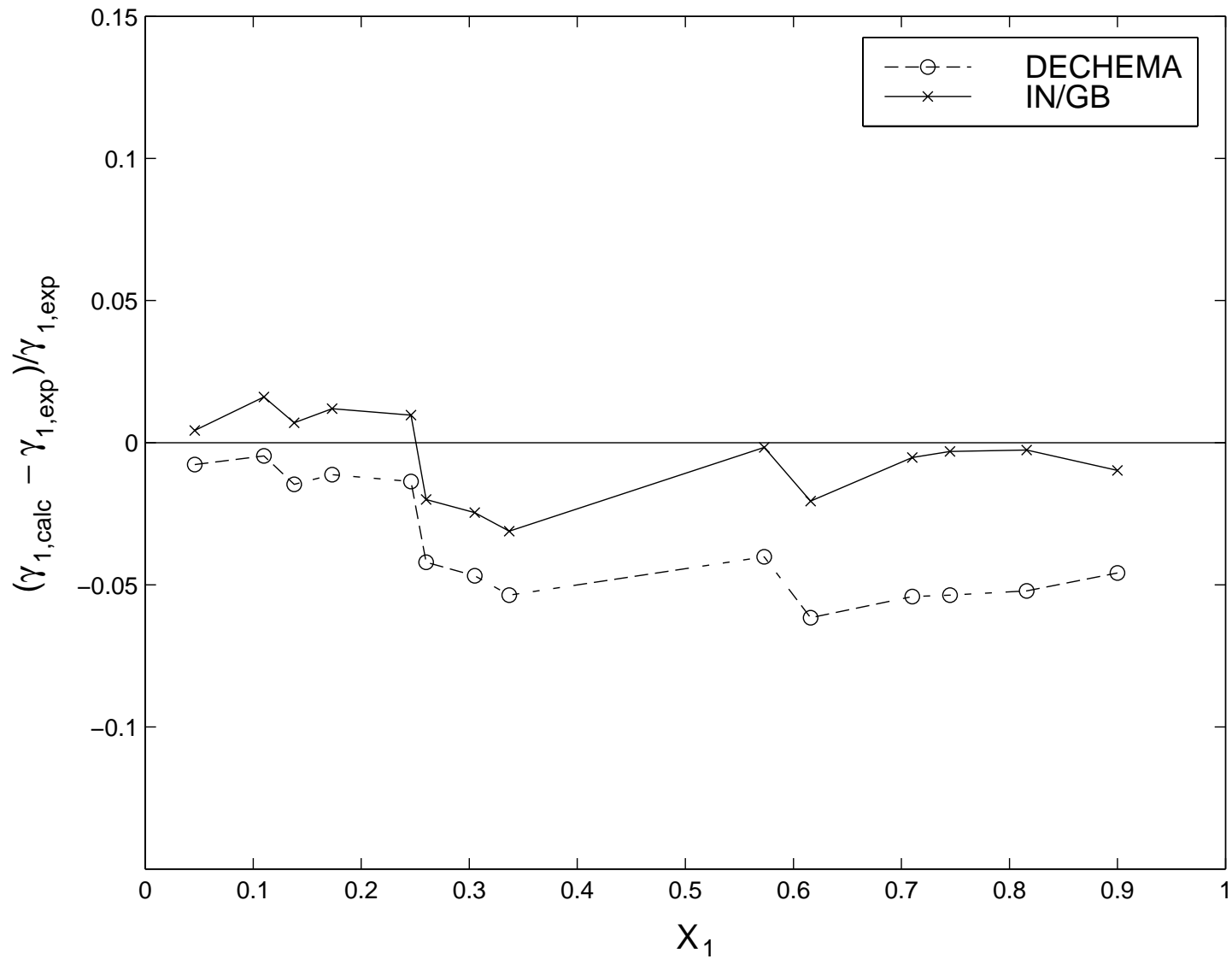
Figure 6: The relative error in Problem 2 (data set 6) between calculated and experimental activity coefficients for *tert*-butanol resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB.
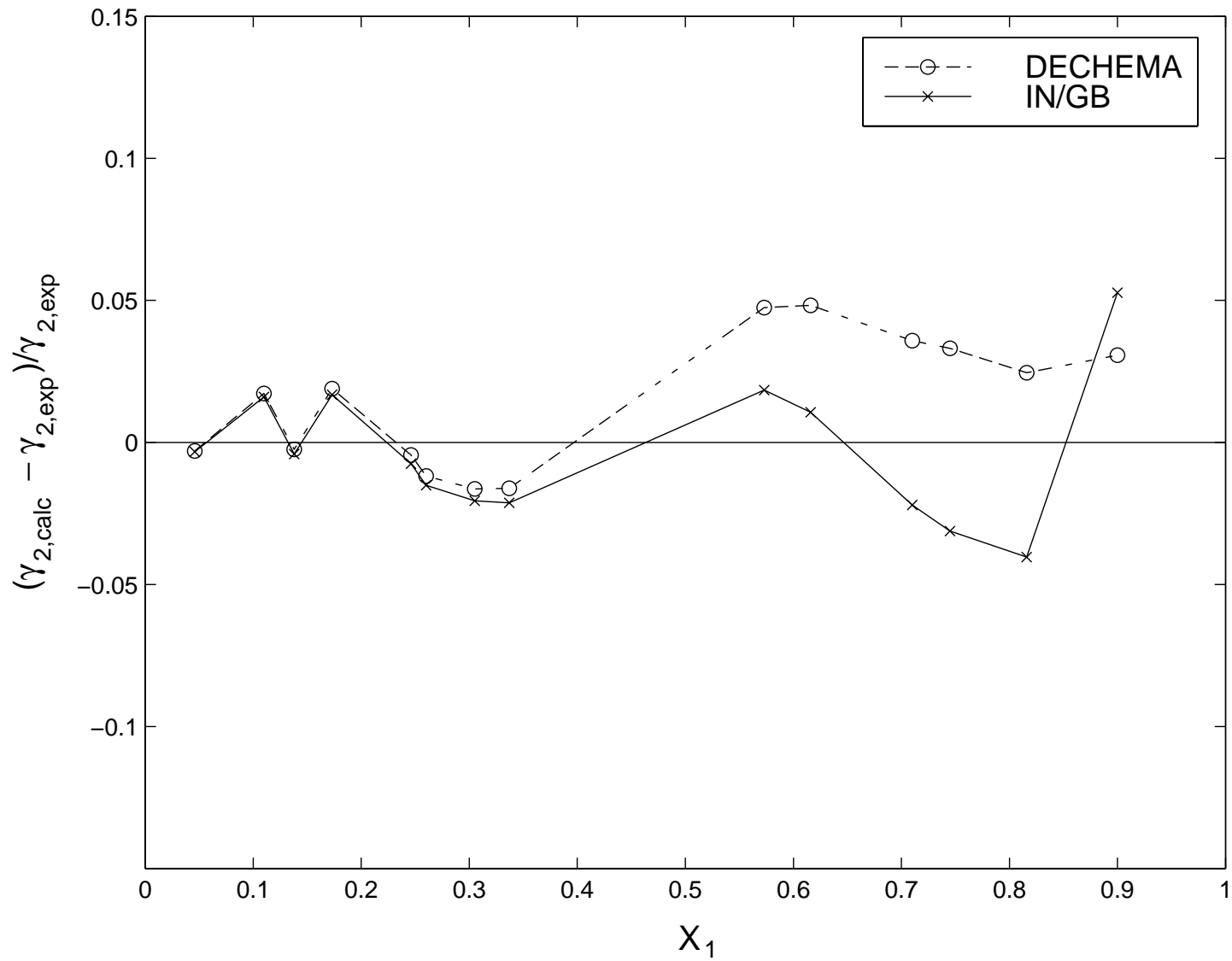
Figure 7: The relative error in Problem 2 (data set 6) between calculated and experimental activity coefficients for 1-butanol resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB.
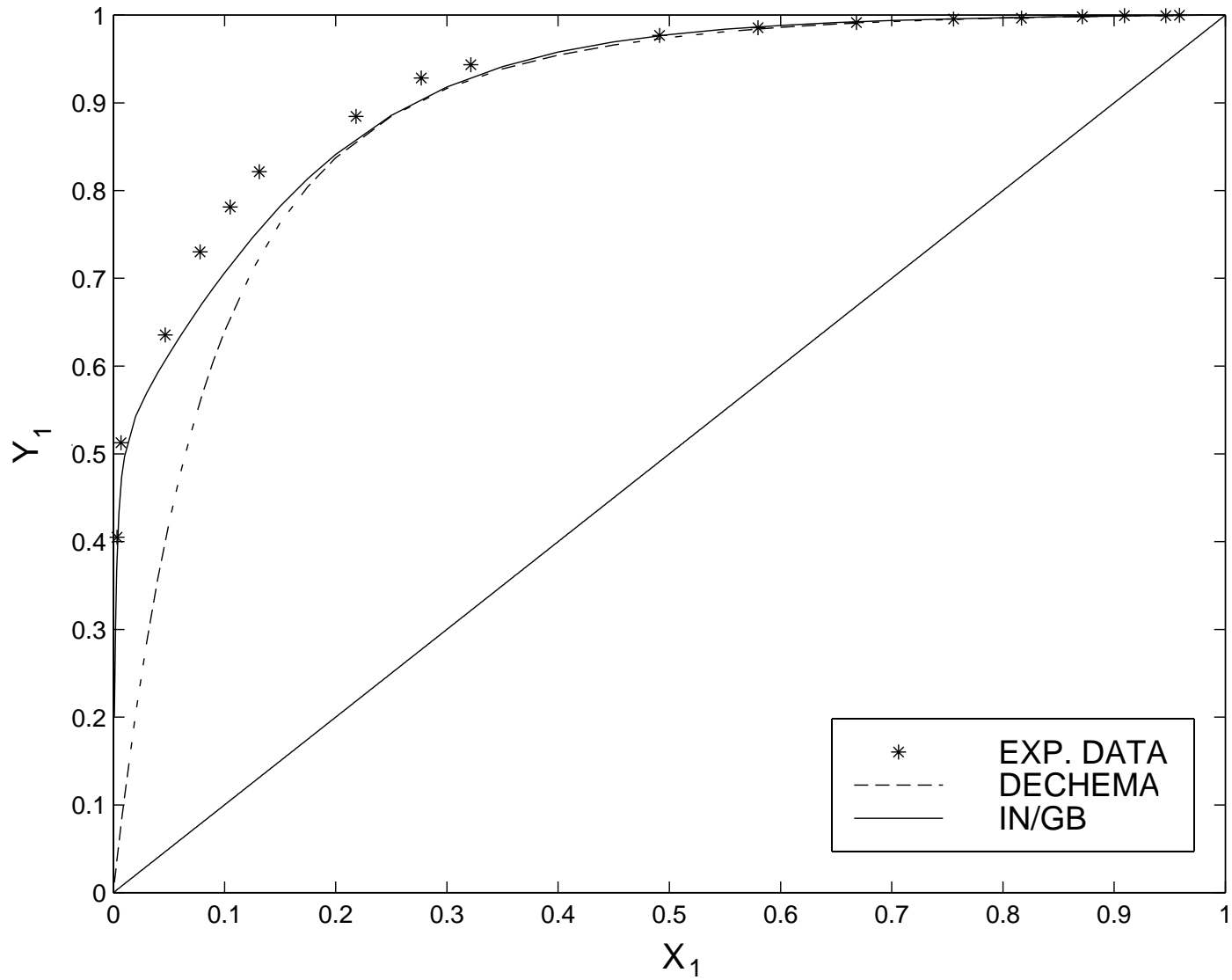
Figure 8: Comparison of VLE prediction for water(1) – 1,2-ethanedial(2) in Problem 3 resulting from the locally optimal parameters values found in DECHEMA and the globally optimal values found using IN/GB.