

# Thermodynamic Calculations Using a Simulated Annealing Optimization Algorithm

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*This paper reports the application and evaluation of a Simulated Annealing - type stochastic optimization method in several thermodynamic calculations for Chemical Engineering. This method is a modified version of the Direct Search Simulated Annealing proposed by Ali et al. [12] which is a memory-based algorithm that associates a set of points with a Markov chain and uses a probabilistic point generation mechanism. It uses a modified Metropolis criterion and an adaptive cooling schedule. Until now, it has been successfully applied in phase stability analysis of non-reacting and reacting mixtures. Considering these results, we have decided to extend the application of this optimization method for other thermodynamic calculations. Its reliability and efficiency are tested using phase equilibrium and parameter estimation problems. The obtained results indicate that proposed method is generally robust for the global minimization of the objective functions involved in flash calculations using Gibbs energy minimization and in the calculation of homogeneous azeotropes in non-reactive mixtures. However, this method is not suitable for data correlation in electrolyte systems. Finally, it requires a reasonable computational time for solving these thermodynamic problems.*

*Keywords: Global optimization, Simulated Annealing, Thermodynamic calculations*

In Chemical Engineering, several thermodynamic calculations can be formulated as optimization problems with or without restrictions. As indicated by Henderson et al. [1] the formulation of thermodynamic calculations for optimization problems offers some advantages: a) the use of a robust optimization method, b) the possibility of using a direct optimization method which requires only calculations of the objective function and c) the use of an iterative procedure whose convergence is almost independent on the initial guesses. Some examples of these calculations are phase stability analysis, phase equilibrium problems, parameter estimation in thermodynamic models, calculation of critical points, among others. These problems are non-linear, multivariable and the objective function used as optimization criterion is non-convex with several local optimums. By consequence, its solving with local optimization methods is not reliable because they generally converge to local optimums.

During the last years, the development and application of global optimization strategies have increased in many areas of Chemical Engineering. Global optimization methods can be classified as deterministic and stochastic [2]. The first class offers a guarantee to find the global optimum of the objective function [21, 32, 24]. However, these strategies often require high computational time (generally more time than stochastic methods) and in some cases the problem reformulation is needed. In the other hand, stochastic optimization methods are robust numerical tools that present a reasonable computational effort in the optimization of multivariable functions; they are applicable to ill-structure or unknown structure problems and can be used with all thermodynamic models [3].

Simulated Annealing (SA) and Genetic Algorithm are the most used stochastic optimization methods in engineering applications [2]. Specifically, in the field of thermodynamics, these methods have been used in phase stability and equilibrium calculations [4, 8] and non-linear parameter estimation [9, 11].

Particularly, SA-type optimization methods are very attractive for engineering applications due to its reliability and simplicity in numerical implementation. Until now, several algorithms for SA have developed where its numerical performances (efficiency and reliability) are very different. Considering this fact, it is convenient to apply and test available algorithms with the aim of identifying a robust and efficient method for thermodynamic calculations.

In this work, we study the numerical performance of a Simulated Annealing optimization method in several thermodynamic problems of Chemical Engineering. This method is a modified version of the Direct Search Simulated Annealing proposed by Ali et al. [12] and its reliability and efficiency have been tested in phase equilibrium calculations and in the parameter estimation of thermodynamic models.

## Description of the Stochastic Optimization Method

Simulated Annealing (SA) is a generalization of Monte Carlo methods to find the global optimum of a multivariable function [13]. This algorithm performs a stochastic search in the permissible region of optimization variables. In minimization problems, the variable perturbations that increase the value of objective function are accepted with a probability controlled by Metropolis criterion [14]. These perturbations allow escaping of local optimums. Generally, SA can find the global optimum of multivariable objective

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functions using a reasonable computational effort. Several algorithms have been developed for SA and they differ in the mechanism used to perform perturbations in optimization variables and in the strategies employed to modify algorithm parameters.

Recently, Ali et al. [12] proposed a memory-based Simulated Annealing algorithm that associates a set of points with a Markov chain and uses a probabilistic point generation mechanism. This algorithm starts with  $N$  random points and their functions stored in an array  $A$  and a single starting point of the initial Markov chain. The trial points are generated in a Markov chain using the configuration of  $np + 1$  points stored in  $A$  with a user-defined probability  $P_w$  or using a random point generation mechanism with probability  $1 - P_w$ . For this random mechanism, we use a procedure similar to that of Corana et al. [15]

$$x_{new} = x_{old} + ((u * 2) - 1)VM \quad (1)$$

where  $u$  is a random number between 0 and 1 and  $VM$  is a step length. The generation mechanism of probability  $P_w$  starts with the random selection of  $np$  points  $x_2, \dots, x_{np+1}$  from  $A$  (where  $np < N$ ), excluding the best point of  $A$  with function  $f_1$ . The centroid  $G$  is calculated from  $x_1, x_2, \dots, x_{np}$  where  $x_1$  is the best point in  $A$  and the trial point  $x_{new}$  is given by

$$x_{new} = 2G - x_{np+1} \quad (2)$$

We use arbitrarily four random points selected from  $A$  to calculate  $G$  ( $np = 4$ ). If  $x_{new}$  falls outside the search space, the random selection process of  $np$  points and the calculation of  $x_{new}$  are repeated until  $x_{new}$  satisfies the restrictions. If after seven trials calculating  $x_{new}$  using  $G$ , we do not find a  $x_{new}$  that falls inside the search space, we calculate the new point using the mechanism provided in eq. (1). The new point is accepted or rejected using a modified Metropolis criterion

$$M(T_{SA}) = \min\{1, \exp(-(f_{new} - f_h)/T_{SA})\} \quad (3)$$

where the trial function value  $f_{new}$  is compared with the worst function value in  $A$  ( $f_h$ ). The accepted point replaces the worst point in  $A$  and the new best and worst points are found in  $A$  before the process continues. This process continues until the Markov chain ends. The length of the Markov chain is

$$L_i = NT + \lfloor NT * F \rfloor \quad (4)$$

where  $L_i$  is the length of Markov chain and  $NT$  is the iteration number before annealing temperature reduction proposed by the user. The function  $F$  is

$$F = 1 - \exp[-(f_h - f_i)] \quad (5)$$

In accordance with Ali et al. [12], this strategy allows increasing the number of function evaluations at a given annealing temperature if the difference between  $f_h$  and  $f_i$  increases. They proposed that generating a point whose function value is less than  $f_i$  ends the current Markov chain. We have tested this strategy in preliminary calculations, and we found that it converges prematurely to local optimums of the objective function. In this work, we use a full Markov chain and the cooling schedule is defined by

$$T_{SA_{j+1}} = (RT)T_{SA_j} \quad (6)$$

where the annealing temperature reduction factor  $RT$  is 0.85. This algorithm (DSAM) stops when the difference between  $f_h$  and  $f_i$  is less than a specified tolerance. In this work, the tolerance value is defined as 1.0E-06. We have implemented this method in a FORTRAN® subroutine, which is available upon request.

Until now, this method has been successfully applied in phase stability analysis of non-reacting and reacting mixtures [8]. Results reported by Bonilla-Petriciolet et al. [8] indicate that this method appears to be robust in the global minimization of multivariable functions. Considering this fact, we have decided to extend the application of DSAM method for other thermodynamic calculations.

Finally, the values used for the principal parameters of DSAM are reported in table 1, which were obtained from the results of phase stability calculations reported by Bonilla-Petriciolet et al. [8].

## Results and discussion

To test the numerical performance (efficiency and reliability) of the optimization method, several thermodynamic problems are considered. Specifically, we have used examples of phase equilibrium calculations and data correlation in thermodynamic models. These problems are multivariable, highly non-linear and its objective function is non-convex with several local optimums. Since stochastic optimization methods do not give an accurate global minimum, we have considered that

**Table 1**  
SUGGESTED VALUES FOR THE PRINCIPAL PARAMETERS OF DSAM  
OPTIMIZATION METHOD

Parameter description	Suggested value <sup>1</sup>
Initial annealing temperature of DSAM, $T_{SA_0}$	10
Probability of point generation mechanism, $P_w$	0.2
Size of array $A$	$5(n_{var} + 1)$
Iteration number before annealing temperature reduction, $NT$	$5n_{var}$

<sup>1</sup>  $n_{var}$  is the overall number of optimization variables. These values were obtained from phase stability calculations in reacting and non-reacting mixtures (Bonilla-Petriciolet et al. [8]).

**Table 2**  
 NUMERICAL PERFORMANCE OF DSAM OPTIMIZATION METHOD IN PHASE STABILITY CALCULATIONS OF NON-REACTIVE MIXTURES

System	Global optimum	Numerical performance <sup>1</sup>		
		SR, %	NFEV	ADD, %
<i>N<sub>2</sub>-C<sub>1</sub>-C<sub>2</sub> at 270 K and 7,600 KPa</i> <i>z (0.25, 0.2, 0.55)</i>	$x^{est}$ (0.1193826, 0.141070, 0.7395473) TPDF = -7.2874E-03	100	81694	0.0162
<i>C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub>-C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub>-C<sub>8</sub>-C<sub>9</sub>-C<sub>10</sub> at 353 K and 38,500 KPa</i> <i>z (0.6598, 0.09084, 0.04726, 0.03509, 0.01492, 0.01657, 0.1047, 0.03082)</i>	$x^{est}$ (0.7705264, 0.0906225, 0.0404649, 0.0265957, 0.0102601, 0.010172, 0.0471032, 0.00425517) TPDF = -1.7220E-03	100	752877	0.1190
<i>C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub>-C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub>-C<sub>8</sub>-C<sub>9</sub>-C<sub>10</sub> at 162.2 °C and 18,900 KPa</i> <i>z (0.6436, 0.0752, 0.0474, 0.0412, 0.0297, 0.0138, 0.0303, 0.0371, 0.0415, 0.0402)</i>	$x^{est}$ (0.5891400, 0.0736340, 0.0486725, 0.0443686, 0.0334250, 0.0162022, 0.0370671, 0.0472301, 0.0549546, 0.0553060) TPDF = -1.017E-04	100	1161863	0.1087

<sup>1</sup> SR is the success rate of finding the global minimum given as percent of calculations performed that satisfies Eq. (7). NFEV is the mean total number of function evaluations during the optimization procedure and ADD is the mean absolute percentage deviation of the calculated variables from the known variables at global minimum. NFEV and AAD are calculated considering only the successful calculations. These results are based on 25 trials performed with random initial values and random number seeds.

the global minimization of the objective function is successful upon satisfying the condition

$$|OBJ_{calc} - OBJ_{min}| < OBJ_{min} * 10^{-4} + 10^{-5} \quad (7)$$

where  $OBJ_{min}$  is the known global minimum of the objective function and  $OBJ_{calc}$  is the calculated value with the optimization method, respectively. This criterion has been used for several researchers to judge the success of a trial in the context of global optimization using stochastic methods [3, 16, 17].

All examples used in this work are solved 25 times (each time with different random initial value and random number seed). The reliability and efficiency of DSAM method is tested considering the next criterions

- Success rate (SR) of finding the global minimum given as percent of calculations performed that satisfies eq. (7).
- Mean total number of function evaluations (NFEV) during the optimization procedure.
- Mean absolute percentage deviation of the calculated variables from the known variables at global minimum

$$AAD = \frac{100}{n_{opt}} \sum_{j=1}^{n_{opt}} \left| \frac{x_j^{min} - x_j^{calc}}{x_j^{min}} \right| \quad (8)$$

where  $x_j^{min}$  is the known global optimum value for the  $j$  variable,  $x_j^{calc}$  is the calculated global optimum value for the  $j$  variable using the stochastic method and  $n_{opt}$  is the overall number of optimization variables, respectively. Parameters NFEV and AAD are calculated considering only the successful calculations. Also, computational time is reported for all examples where the calculations were performed on a Processor Intel Pentium M 1.73GHz with 504 MB of RAM.

#### Problem 1. Phase stability analysis in non-reactive mixtures

Phase stability analysis is a fundamental procedure in phase equilibrium calculations for multicomponent and multiphase systems [4]. Baker et al. [18] and Michelsen [19] showed that phase stability of a mixture of  $c$

components with a global composition  $z = \{z_1, \dots, z_c\}$ , at constant temperature and pressure, results from global minimization of the Tangent Plane Distance Function (TPDF)

$$TPDF = \sum_{i=1}^c y_i \left( \mu_{i|y} - \mu_{i|z} \right) \quad (9)$$

where  $\mu_{i|y}$  and  $\mu_{i|z}$  are the chemical potentials of component  $i$  calculated at compositions  $y$  and  $z$ , respectively. The mixture  $z$  is unstable if the global minimum of TPDF is lower than 0. Global minimization of TPDF is a difficult task and requires robust numerical methods because this function is multivariable, non-convex and highly nonlinear. By consequence, phase stability problems are useful to test the numerical performance of DSAM method. As mentioned before, Bonilla-Petriciolet *et al.* [8] tested the numerical performance of DSAM in phase stability calculations in reactive and non-reactive mixtures. In this work, we have included this example only with illustrative purposes. Therefore, three non-reacting mixtures with different feed conditions are considered in phase stability calculations. These systems have been studied by Hua et al. [20] Harding and Floudas [21] and Henderson *et al.* [5] for testing deterministic and stochastic global optimization methods in phase stability analysis. Global minimization of TPDF is performed with respect to  $c$  mole numbers where the admissible region for all mole numbers is  $n_i \in (0,1) \quad i=1, \dots, c$ . Thermodynamic properties of all mixtures are calculated using SRK EoS with conventional mixing rules. Parameters of pure components are taken from Reid *et al.* [22]. Interaction parameters for the ternary mixture are given by  $k_{N_2C_1} = 0.038$ ,  $k_{N_2C_2} = 0.08$  and  $k_{C_1C_2} = 0.021$  while for others mixtures all interaction parameters are zero. Results of phase stability calculations are reported in table 2. For all mixtures, DSAM method is very reliable to find the global minimum of TPDF. Of course, the computational effort increases when the number of component also increases. ADD value is lower than 0.12% for all mixtures. Our phase stability results are consistent

**Table 3**  
 NUMERICAL PERFORMANCE OF DSAM OPTIMIZATION METHOD IN PHASE EQUILIBRIUM  
 CALCULATIONS NON-REACTIVE MIXTURES

System	Global optimum	Numerical performance <sup>1</sup>		
		SR, %	NFEV	ADD, %
$C_1 - C_2 - C_3 - iC_4 - C_4 - iC_5 - C_5 - C_6 - iC_{15}$ at 19.84 atm and 314 K $z$ (0.614, 0.10259, 0.04985, 0.00898, 0.02116, 0.00722, 0.01187, 0.01435, 0.16998)	$x^\alpha$ (0.083652, 0.054879, 0.061769, 0.017338, 0.04676, 0.020578, 0.035595, 0.049032, 0.630398) $x^\beta$ (0.809794, 0.120204, 0.04545, 0.005895, 0.011709, 0.002288, 0.003111, 0.001546, 0.000003) $g = -0.76977$	100	917690	0.5271
$C_2 - C_3 - C_4 - C_5 - C_6$ at 390 K and 5580 KPa $z$ (0.39842, 0.29313, 0.20006, 0.07143, 0.03696)	$x^\alpha$ (0.388312, 0.292671, 0.204643, 0.074785, 0.039589) $x^\beta$ (0.404765, 0.293418, 0.197183, 0.069324, 0.03531) $g = -1.18678$	100	252470	0.5105
$H_2O - CO_2 - 2-propanol - Ethanol$ at 350 K and 2250 KPa $z$ (0.03154, 0.9328, 0.02311, 0.01255)	$x^\alpha$ (0.020032, 0.943893, 0.023384, 0.01269) $x^\beta$ (0.997388, 0.001732, 0.000083, 0.00797) $g = -0.09314$	12	142905	0.0141

<sup>1</sup> SR is the success rate of finding the global minimum given as percent of calculations performed that satisfies Eq. (7), NFEV is the mean total number of function evaluations during the optimization procedure and ADD is the mean absolute percentage deviation of the calculated variables from the known variables at global minimum. NFEV and AAD are calculated considering only the successful calculations. These results are based on 25 trials performed with random initial values and random number seeds.

with those reported by Hua *et al.* [20], Harding and Floudas [21] and Henderson *et al.* [5].

### Problem 2. Gibbs energy minimization in non-reacting mixtures

Phase equilibrium calculation is a recurrent and important element in the simulation of separation processes. Basically, this problem can be formulated as the global minimization of the total Gibbs energy of the system under analysis. For a non-reacting multiphase mixture, the objection function that must be optimized is given by

$$g = \sum_{k=\alpha}^{\pi} n^k g^k \quad (10)$$

subject to  $n^T = \sum_{k=\alpha}^{\pi} n^k$  where  $g$  is the total Gibbs energy of

mixing,  $n^k$  is the total mole number at phase  $k$  and  $g^k$  is the Gibbs energy of mixing of phase  $k$ , respectively. Until now, several local and global optimization methods have proposed and tested in the global minimization of Gibbs energy for phase equilibrium calculations [23]. However, when phase equilibrium calculations are performed with conventional optimization methods, we have initialization problems and we also can converge to trivial solutions or unstable equilibrium states that correspond to local minimums of Gibbs energy [23]. In accordance with Rangaiah [6], Gibbs energy function can be minimized with respect to a set of  $c$  independent variables  $\chi_i$  inside the interval  $[0, 1]$ . The introduction of these variables eliminates the restrictions imposed by material balances, reduces problem dimensionality and the optimization problem is transformed to an unconstrained one. For a flash calculation (two phase equilibrium), these optimization variables are related to mole numbers using the following expressions

$$n_i^\alpha = n_i^z \chi_i \quad i = 1, \dots, c \quad (11)$$

$$n_i^\beta = n_i^z - n_i^\alpha \quad i = 1, \dots, c \quad (12)$$

being  $n_i^\alpha$  and  $n_i^\beta$  the equilibrium mole numbers of component  $i$ . Rangaiah [6], Rangaiah and Teh [3], Rangaiah and Teh [23] and Srinivas and Rangaiah [24] have tested the numerical performance of different stochastic optimization methods (Simulated Annealing, Genetic Algorithms, Tabu Search and Random Tunneling) in phase equilibrium calculations using this approach. In this work, three mixtures are considered for testing DSAM method in Gibbs energy minimization based on Rangaiah's approach. All thermodynamic properties are calculated using SRK EoS with conventional mixing rules where the parameters of pure components are taken from Reid *et al.* [22]. All interaction parameters are zero. In table 3 we report the results of phase equilibrium calculations. For two mixtures, DSAM method is very reliable to find the equilibrium compositions. However, in the quaternary mixture, proposed method fails several times in the global minimization of Gibbs energy. Harding and Floudas [21] have used this mixture for evaluating a deterministic global optimization method in phase stability analysis and they have indicated that this mixture is a challenging system whose phase behavior is complex. In the other hand, ADD value is lower than 0.6% for all mixtures and NFEV ranged from 142905 to 917690, respectively. Results of phase equilibrium are consistent with data reported by Rangaiah [6] and Harding and Floudas [21].

### Problem 3. Parameter estimation for vapor-liquid equilibrium modeling based on least squares and maximum likelihood approaches

Parameter estimation is a common problem in many engineering applications and, in the context of

thermodynamics, it may also present computational difficulties due to the possibility of several local optimums in the objective function used as optimization criterion. As indicated by Dominguez et al. [25], failing to identify the global optimum in parameter estimation may cause errors and uncertainties in equipment design and erroneous conclusions about model performance. Recently, some papers have reported the application of stochastic optimization methods in parameter estimation using chemical engineering models [26, 29]. In first instance, we have considered the data correlation of vapor-liquid equilibrium for the binary system tert butanol - 1 butanol. This system was studied by Gau et al. [30] using an interval analysis approach and the classical least square formulation. Also, Bonilla-Petriciolet et al. [29] have tested the numerical performance of the Simulated Annealing method proposed by Corana et al. [15] in data correlation of this system. We use three sets of experimental data at different isobaric conditions and they were taken from DECHEMA [31]. Wilson equation is used to calculate the liquid phase activity coefficients, which are defined by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (13)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (14)$$

The binary parameters  $\Lambda_{12}$  and  $\Lambda_{21}$  are given by

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left(-\frac{\theta_1}{RT}\right) \quad (15)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left(-\frac{\theta_2}{RT}\right) \quad (16)$$

where  $v_1$  and  $v_{12}$  are the pure component liquid molar volumes,  $T$  is the system temperature,  $\theta_1$  and  $\theta_2$  are the energy parameters, respectively. Assuming an ideal vapor phase, the experimental values for the activity coefficients  $\gamma_{\text{exp}}^i$  are calculated using the next expression

$$\gamma_i^{\text{exp}} = \frac{y_i^{\text{exp}} P^{\text{exp}}}{x_i^{\text{exp}} P_i^0} \quad i = 1, \dots, c \quad (17)$$

where  $P_i^0$  is the vapor pressure of pure component  $i$  at the system temperature  $T$  and  $c$  is the number of components, respectively. The vapor pressure is calculated using

$$\log_{10} P_i^0 = a_i - \frac{b_i}{c_i + T} \quad (18)$$

where  $T$  is in  $^{\circ}\text{C}$  and  $P_i^0$  in mmHg. Parameters for vapor pressure calculation are also taken from DECHEMA [31]. We have used a relative least squares formulation to fit the data

$$F_{\text{obj}} = \sum_{j=1}^{\text{ndat}} \sum_{i=1}^c \left( \frac{\gamma_{ij}^{\text{exp}} - \gamma_{ij}^{\text{calc}}}{\gamma_{ij}^{\text{exp}}} \right)^2 \quad (19)$$

This function is minimized with respect to the Wilson model parameters inside the intervals  $\theta_1 \in (-8500, 320000)$  and  $\theta_2 \in (-8500, 320000)$ . Results of parameter estimation for this system are reported in table 4. For all data sets, the success rate of DSAM method ranged from 60 to 68%, respectively. Despite that this problem has only two optimization variables, its objective function is challenging for DSAM method. With respect to efficiency, the numerical effort of DSAM is similar for the three tested conditions where NFEV(33228, 39319) and ADD is lower than 0.15% for all cases. The global optimums reported in table 4 are consistent with the results reported by Gau et al. [30] and Bonilla-Petriciolet et al. [29].

In our second case, we have considered the error-invariable parameter estimation using the van Laar model for liquid phase in the correlation of experimental vapor-liquid equilibrium data of binary system methanol - 1,2 dichloroethane. This system was studied by Esposito and Floudas [32] using a deterministic global optimization method and by Bonilla-Petriciolet et al. [29] using the Simulated Annealing method of Corana et al. [15]. The experimental data consists of five points for the state variables: pressure in mmHg, temperature in Kelvin, liquid

**Table 4**  
NUMERICAL PERFORMANCE OF DSAM OPTIMIZATION METHOD IN DATA CORRELATION OF VAPOUR-LIQUID EQUILIBRIUM OF THE BINARY SYSTEM TERT BUTANOL-1 BUTANOL USING LEAST SQUARES

		<i>formulation</i>			
		<i>Numerical performance</i> <sup>1</sup>			
<i>P, mm Hg</i>	<i># Data</i>	<i>Global optimum</i>	<i>SR, %</i>	<i>NFEV</i>	<i>ADD, %</i>
100	9	$\theta_1 = -568$ $\theta_2 = 745.3$ $F_{\text{obj}} = 0.0103$	60	39319	0.1233
500	9	$\theta_1 = -718$ $\theta_2 = 1264.7$ $F_{\text{obj}} = 0.0069$	68	36711	0.1080
700	9	$\theta_1 = -734$ $\theta_2 = 1318.2$ $F_{\text{obj}} = 0.0137$	60	33228	0.0382

<sup>1</sup> SR is the success rate of finding the global minimum given as percent of calculations performed that satisfies Eq. (7), NFEV is the mean total number of function evaluations during the optimization procedure and ADD is the mean absolute percentage deviation of the calculated variables from the known variables at global minimum. NFEV and AAD are calculated considering only the successful calculations. These results are based on 25 trials performed with random initial values and random number seeds.

**Table 5**  
 NUMERICAL PERFORMANCE OF DSAM OPTIMIZATION METHOD IN THE CALCULATION OF  
 HOMOGENEOUS AZEOTROPES IN NON-REACTING MIXTURES

System	Global optimum	SR, %	NFEV	ADD, %
Benzene – Isopropanol at 1 atm NRTL model and Ideal gas. Model parameters are given by Maier <i>et al.</i> <sup>35</sup>	$x^{azeo}$ (0.58770, 0.4123) 71.832 °C	100	13095	0.00
Acetone – Chloroform - Methanol - Benzene at 1 atm NRTL model and Ideal gas. Model parameters are given by Maier <i>et al.</i> <sup>35</sup>	$x^{azeo}$ (0.356902, 0.165492, 0.427351, 0.050256) 57.045 °C	100	271226	0.05
CO <sub>2</sub> - Ethane at 1730.445 KPa SRK EoS with conventional mixing rules. Model parameters are given by Lucia <i>et al.</i> <sup>38</sup>	$x^{azeo}$ (0.652211, 0.347789) 243.15 K.	100	15049	0.00
Chloroform - Ethanol at 55°C Margules model and Virial equation. Model parameters are given by Smith and Van Ness <sup>39</sup>	$x^{azeo}$ (0.840888, 0.159112) 86.747 KPa.	100	13231	0.00

<sup>1</sup> SR is the success rate of finding the global minimum given as percent of calculations performed that satisfies Eq. (7), NFEV is the mean total number of function evaluations during the optimization procedure and ADD is the mean absolute percentage deviation of the calculated variables from the known variables at global minimum. NFEV and AAD are calculated considering only the successful calculations. These results are based on 25 trials performed with random initial values and random number seeds.

and vapor mole fractions of methanol, respectively. The vapor pressure of pure components are calculated using

$$P_i^0 = \exp\left(a_i - \frac{b_i}{T - c_i}\right) \quad (20)$$

where  $a_i$  is given in mmHg,  $T$  in Kelvin and the constants of Antoine equation are taken from Esposito and Floudas [32], respectively. The activity coefficients are defined by

$$\gamma_1 = \exp\left[\frac{A}{RT} \left(1 + \frac{A x_1}{B x_2}\right)^{-2}\right] \quad (14)$$

$$\gamma_2 = \exp\left[\frac{B}{RT} \left(1 + \frac{B x_2}{A x_1}\right)^{-2}\right] \quad (22)$$

We use an unconstrained optimization formulation in the data fitting procedure. Based on Esposito and Floudas [32] and Gau and Stadther [33], the temperature is scaled by a reference temperature  $T_r = 323.15$  K and the van Laar model parameters are also defined considering the

reference temperature as  $\vec{\theta} = \left(\frac{A}{RT_r}, \frac{B}{RT_r}\right)$ . The state

variables of the system are  $\left(x_1, y_1, P, \frac{T}{T_r}\right)$  and their standard deviations are defined as (0.005, 0.015, 0.75, 0.000309). The objective function is given by

$$F_{obj} = \sum_{i=1}^{ndat} \left[ \frac{(x'_{1i} - x_{1i})^2}{\sigma_{x_1}^2} + \frac{(y'_{1i} - y_{1i})^2}{\sigma_{y_1}^2} + \frac{(P'_i - P_i)^2}{\sigma_P^2} + \frac{(TS'_i - TS_i)^2}{\sigma_{TS}^2} \right] \quad (23)$$

where  $TS = T / T_r$ . Equations (24) and (25) are used to eliminate  $y_1$  and  $P$  in the objective function and to transform the problem as unconstrained optimization

$$P = \gamma_1 x_1 P_1^0 + \gamma_2 (1 - x_1) P_2^0 \quad (24)$$

$$y_1 = \frac{\gamma_1 x_1 P_1^0}{\gamma_1 x_1 P_1^0 + \gamma_2 (1 - x_1) P_2^0} \quad (25)$$

For this case, we have twelve optimization variables where the initial intervals on the independent state variables  $\vec{z}^i = \left(x_1^i, T^i\right)$  are set using plus and minus three standard deviations. For the case of van Laar model parameters, we use  $A/RT \in (1, 2)$  and  $B/RT \in (1, 2)$  as initial intervals for the optimization of objective function. In all calculations performed, DSAM is capable of finding the global minimum of objective function without numerical problems. It is important to note that in this example, the reliability of DSAM is not affected by the increment in the number of optimization variables. The global minimum is = 3.326 where van Laar parameters are given by  $A/RT = 1.912$  and  $B/RT = 1.608$ , respectively. DSAM method showed a  $NFEV = 1926036$  and  $ADD = 0.00042\%$ . Our results are consistent with Gau and Stadther<sup>33</sup> and Bonilla-Petriciolet *et al.* [29].

#### Problem 4. Calculation of homogeneous azeotropes in non-reactive mixtures

Homogeneous azeotropy is a condition of vapor-liquid equilibrium in which the composition is identical on both phases. The description of this phase equilibrium condition is essential for the selection of strategies in shynthesis, design and operation of separation processes. This description consists of establishing the temperature, pressure and composition as well as the component number of the azeotrope. Traditional methods for the calculation of homogeneous azeotropes use local procedures and different objective functions employing fugacity coefficients or relative volatilities. Recently, some reliable techniques have been proposed to calculate homogeneous azeotropy

which are principally based on deterministic strategies [34-36]. To the best of the authors's knowledge, Bonilla-PetricioleT [37] has introduced the application of a stochastic optimization approach to calculate homogeneous azeotropes. The thermodynamic conditions that a homogeneous azeotrope should satisfy are given by

$$\mu_i^\alpha - \mu_i^\beta = 0 \quad i = 1, \dots, c \quad (26)$$

where  $\mu_i$  is the chemical potential of component  $i$ . Equation (26) is a system of  $c$  nonlinear equations with  $c-1$  unknown compositions  $x_i^{\text{azeo}}$  plus the unknown temperature or pressure of the azeotrope. We can solve these equations as an optimization problem by minimizing

$$F_{\text{obj}} = \sum_{i=1}^c [\mu_i^\alpha - \mu_i^\beta]^2 \quad (27)$$

Here we find the mole fractions (for  $c = 2$ ) or mole numbers (for  $c \geq 3$ ), temperature or pressure that corresponds to the global minimum of this objective function ( $F_{\text{obj}}=0$ ). We have calculated the homogeneous azeotropes for different mixtures previously reported in literature using DSAM method. Solution models and equations of state are used to calculate thermodynamic properties of our examples (table 5). Initial intervals for systems benzene - isopropanol and acetone - chloroform - methanol - benzene are  $n_i^{\text{azeo}} (0, 1)$  for  $i = 1, \dots, c$  and  $T \in (10, 100)^\circ\text{C}$  while for systems  $\text{CO}_2$  - ethane and chloroform - ethanol we use  $x_i^{\text{azeo}} \in (0, 1)$ ,  $T \in (220, 260)\text{K}$  and  $\text{KPa}$ , respectively. Results of azeotropy calculations are also reported in table 5. Our calculations show that DSAM method is very reliable to find the homogeneous azeotropes in all examples even using EoS as thermodynamic model. It is convenient to note that the available deterministic methods for the calculation of homogeneous azeotropes have been applied only with solution models and ideal gas behavior [34, 35]. However, this optimization strategy can be used with any thermodynamic model without the reformulation of thermodynamic problem. With respect to efficiency, NFEV ranged from 13095 to 271226 while ADD is lower than 0.05 % for all examples. Our results of azeotropy calculations agree with those of Harding et al. [34], Maier et al. [35], Smith and Van Ness [38] and Lucia et al. [39].

#### Problem 5. Data fitting of activity coefficients in electrolyte systems

Thermodynamic properties of aqueous electrolyte systems have been widely studied due to their applications in chemical industry, water pollution control, bioseparations, food processing and oilfield operation.

Several models have been proposed to correlate the properties of electrolyte solutions [40]. Generally, developed models can fit and predict the activity coefficients of electrolytes using few adjustable parameters. However, the non-linearity of thermodynamic models may cause computational difficulties in the parameter estimation due to the possibility of several local optimums in the objective function used as optimization criterion. Belvéze et al. [41] have shown that the correlation of activity coefficients in electrolyte solutions is a challenging optimization problem. By consequence, robust and efficient methods are required for this issue. The stochastic optimization methods are attractive alternatives to solve this problem. In this example, we have used the NRTL-electrolyte model proposed by Chen et al. [42] to fit the experimental data of activity coefficients of aqueous electrolyte solutions. This model is easy to use and works very well for several simple salts where a complete dissociation of the electrolyte existS [41]. The model is conformed by two terms

$$\ln(\gamma_i) = \ln(\gamma_i^{\text{PDH}}) + \ln(\gamma_i^{\text{NRTL}}) \quad (28)$$

where  $\gamma_i$  is the activity of component  $i$  in the solution,  $\gamma_i^{\text{PDH}}$  is the activity coefficient of component  $i$  due to coulombic forces and  $\gamma_i^{\text{NRTL}}$  is the NRTL contribution to the activity coefficient of component  $i$ , respectively. The activity coefficient  $\gamma_i^{\text{PDH}}$ , which is a Debye-Hückel term, is given by

$$\ln(\gamma_i^{\text{PDH}}) = - \frac{1000}{M_{\text{solvent}}} A_\phi \left( \frac{2Z_i^2}{\rho} \ln(1 + \rho I^{0.5}) + \frac{Z_i^2 I^{0.5} - 2I^{1.5}}{1 + \rho I^{0.5}} \right) \quad (29)$$

The closest approach parameter  $\rho$  is equal to 14.9 for all componentS [42] and  $M_{\text{solvent}}$  is the solvent molecular weight. The ionic strength  $I$  depends on the charge of each ions  $Z_i$  and its mole fraction  $x_i$  then

$$I = \frac{1}{2} \sum_i Z_i^2 x_i \quad (30)$$

In this case, parameter  $A_\phi$  is calculated using the following correlation proposed by Chen et al. [42]

$$A_\phi = -61.44534 \exp\left(\frac{T-273.15}{273.15}\right) + 2.864468 \left( \exp\left(\frac{T-273.15}{273.15}\right) \right)^2 + 183.5379 \ln\left(\frac{T}{273.15}\right) - 0.6820223 (T-273.15) + 0.0007875695 (T^2 - 273.15^2) + 58.95788 \left(\frac{273.15}{T}\right) \quad (31)$$

Table 6

NUMERICAL PERFORMANCE OF DSAM OPTIMIZATION METHOD IN THE DATA CORRELATION OF MEAN ACTIVITY CORFFICIENTS OF AQUEOUS ELECTROLYTE SOLUTIONS USING NRTL-ELECTROLYTE MODEL GLOBAL MINIMUM<sup>1</sup>

Compound	Global minimum <sup>1</sup>					Numerical performance <sup>1</sup>		
	$m_{\text{max}}$	$ndat$	$\tau_{\text{cas}}$	$\tau_{\text{sca}}$	$F_{\text{obj}}$	SR, %	NFEV	ADD, %
$[\text{NH}_4^+][\text{CH}_3\text{SO}_3^-]$	4.0	13	-4.1047	7.9978	2.95E-05	0	-	-
$[(\text{C}_4\text{H}_9)_4\text{N}^+][\text{C}_2\text{H}_5\text{SO}_3^-]$	4.0	13	-3.4530	5.8167	6.13E-02	100	42469	0.05
$\{(\text{CH}_3)_3(\text{C}_6\text{H}_5)\text{N}^+[\text{Cl}^-]$	8.0	25	-4.3242	9.3821	1.75E-03	64	37130	0.00
$\{(\text{CH}_3)_4\text{N}^+[\text{Br}^-]$	5.5	22	-4.2846	8.9783	6.20E-03	4	34295	0.00

<sup>1</sup> SR is the success rate of finding the global minimum given as percent of calculations performed that satisfies Eq. (7), NFEV is the mean total number of function evaluations during the optimization procedure and ADD is the mean absolute percentage deviation of the calculated variables from the known variables at global minimum. NFEV and AAD are calculated considering only the successful calculations. These results are based on 25 trials performed with random initial values and random number seeds.

**Table 7**  
COMPUTATION TIME REQUIRED FOR THERMODYNAMIC CALCULATIONS USING DSAM  
OPTIMIZATION METHOD

Problem	System	Time, seconds
1.- Phase Stability Analysis	$N_2-C_1-C_2$	0.8
	$C_1-C_2-C_3-C_4-C_5-C_6-C_7-16-C_{17}$	12.4
	$C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8-C_9-C_{10}$	22.6
2.- Gibbs Energy Minimization for Phase Equilibrium	$C_1-C_2-C_3-iC_4-C_1-iC_5-C_5-C_6-iC_{15}$	32.7
	$C_2-C_3-C_4-C_5-C_6$	5.4
	$H_2O-CO_2-2-propanol-ethanol$	3.0
3.- Parameter Estimation for VLE modeling	<i>Tert butanol - 1 butanol at 100 mmHg</i>	1.2
	<i>at 500 mmHg</i>	0.9
	<i>at 700 mmHg</i>	0.9
	<i>Methanol - 1,2 dichloroethane</i>	33.9
4- Homogeneous Azeotrope Calculation	<i>Benzene - Isopropanol</i>	0.1
	<i>Acetone - Chloroform - Methanol - Benzene</i>	3.5
	<i>CO<sub>2</sub> - Ethane</i>	0.3
	<i>Chloroform - Ethanol</i>	0.1
5.- Parameter estimation of activity coefficients of electrolytes	$[NH_4^+][CH_3SO_3^-]$	-
	$[(C_4H_9)_4N^+][C_2H_5SO_3^-]$	1.8
	$[(CH_3)_3(C_6H_5)N^+][Cl^-]$	2.9
	$[(CH_3)_4N^+][Br^-]$	1.7

where  $T$  is given in Kelvin. Activity coefficient contributions of NRTL-electrolyte model for cation and anion are calculated using

$$\ln(\gamma_{cation}^{NRTL}) = \frac{\tau_{cas} x_s^2 G_{cas}}{(x_a G_{cas} + x_c G_{cas} + x_s)^2} + \frac{\tau_{sca} Z_c x_s G_{sca}}{x_a + x_s G_{sca}} - \frac{\tau_{sca} Z_a x_a x_s G_{sca}}{(x_s G_{sca} + x_c)^2} - \tau_{cas} G_{cas} - \tau_{sca} Z_c \quad (32)$$

$$\ln(\gamma_{anion}^{NRTL}) = \frac{\tau_{cas} x_s^2 G_{cas}}{(x_a G_{cas} + x_c G_{cas} + x_s)^2} + \frac{\tau_{sca} Z_a x_s G_{sca}}{x_c + x_s G_{sca}} - \frac{\tau_{sca} Z_c x_c x_s G_{sca}}{(x_s G_{sca} + x_a)^2} - \tau_{cas} G_{cas} - \tau_{sca} Z_a \quad (33)$$

where  $G_{cas} = \exp(-\alpha\tau_{cas})$ ,  $G_{sca} = \exp(-\alpha\tau_{sca})$ ,  $\alpha$  is equal to 0.2 and  $c$ ,  $a$  and  $s$  corresponds to cation, anion and solvent, respectively. Parameters  $\tau_{cas}$  and  $\tau_{sca}$  are empirical and they are obtained by fitting the experimental data. According to Belvéze et al. [41], these parameters are subject to the following theoretical expectation:  $\tau_{cas} \leq 0$  and  $\tau_{sca} \geq 0$  where  $|\tau_{cas}| < |\tau_{sca}|$ . Mean activity coefficient  $\gamma_{\pm}$  of the salt in the solution is the experimental quantity that is actually measured. This property is a function of molality  $m$ , solvent molecular weight  $M_{solvent}$ , the stoichiometric coefficients ( $\nu_+$ ,  $\nu_-$ ) obtained from the salt dissociation  $M_+ X_- \leftrightarrow \nu_+ M^{z+} + \nu_- X^{z-}$  and the sum of these stoichiometric coefficients  $\nu$ . So, the mean activity coefficient is obtained from

$$\ln(\gamma_{\pm}) = \frac{1}{\nu} [\nu_+ \ln(\gamma_{cation}) + \nu_- \ln(\gamma_{anion})] - \ln(1 + 0.001 M_{solvent} m \nu) \quad (34)$$

where  $\gamma_{cation}$  and  $\gamma_{anion}$  are calculated from eq. (28). In this study, we use the following objective function to correlate the mean activity coefficient data

$$F_{obj} = \sum_i^{ndat} [\ln(\gamma_{\pm}^{exp})_i - \ln(\gamma_{\pm}^{calc})_i]^2 \quad (35)$$

where  $ndat$  is the overall number of experimental data,  $exp$  and  $calc$  are the experimental and calculated values, respectively. This function has been used by Belvéze et al. [41] and they showed that it is nonconvex and may have multiple local optimums. This function is minimized with respect to  $\tau_{cas}$  and  $\tau_{sca}$ . Data of mean activity coefficients at 25°C for different quaternary ammonium

salts have been used. Experimental information is taken from Gregor et al. [43], Lindenbaum and Boyd [44] and Boyd et al. [45]. All these systems have been fitted by Belvéze et al. [41] using same thermodynamic model, objective function and a deterministic optimization approach based on interval analysis. The objective function was minimized inside the following initials intervals:  $\tau_{cas} \in (-50, 10)$  and  $\tau_{sca} \in (-10, 50)$ , which were proposed by Belvéze et al. [41]. According to them, although physically we should expect  $\tau_{cas} < 0$  and  $\tau_{sca} > 0$ , proposed intervals are useful to identify inadequacies in the model if the globally optimal parameters values are consistently outside the physically expected range. Results of parameter estimation for different electrolyte systems appear in table 6. In general, DSAM shows several failures to find the global minimum in the parameter estimation of NRTL-electrolyte model. Only for one case, DSAM shows a success rate of 100% in data fitting. Our results suggest that DSAM method is not suitable for data correlation of activity coefficients in electrolyte systems. In all electrolytes systems, the optimization method required a mean NFEV value from 34295 to 42469 while ADD is lower than 0.05% for all analyzed systems.

Finally, table 7 reports the mean computational time to find the global minimum for all examples. Computation time ranged from 0.1 to 33.9 s, which is very reasonable to solve the thermodynamic problems considered in this work. It is important to note that numerical effort and computation times reported for DSAM can be reduced if we relax the tolerance value for convergence. In this case, it is convenient to use a local optimization method to refine the solution obtained with DSAM method.

## Conclusions

Reliability and efficiency of a stochastic optimization method has been tested in several thermodynamics calculations related to Chemical Engineering. This method is a modified version of the Direct Search Simulated Annealing proposed by Ali et al. [12]. In general, our results show that proposed method is robust to perform phase stability analysis, two-phase equilibrium calculations using Gibbs energy minimization and the prediction of homogeneous azeotropes. However, it is not suitable for



data correlation in thermodynamic models, especially in electrolyte systems.

Other stochastic optimization methods should be studied with the aim of identifying a reliable and efficiency strategy for thermodynamic calculations in Chemical Engineering.

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## Notation

ADD- mean absolute percentage deviation

A, B- parameters of van Laar model

$a_1, b_1, c_1$  - parameters of Antoine equation

c- number of components

f- objective function

G - centroid

g- total Gibbs energy of mixing

I - ionic strength

$k_{ij}$  - interaction parameter

$M_{solvent}$  - solvent molecular weight

n - mole number

NT- iteration number before temperature reduction

P - Pressure

$P_i^o$  - vapor pressure of pure component

R - universal gas constant

RT- temperature reduction factor

T - Temperature

$T_{SA}$  - annealing temperature

$T_r$  - reference temperature

TPDF - tangent plane distance function

u - random number

v - sum of stoichiometric coefficients

$v_p, v_2$  - pure component liquid molar volumes

x, y - mole fraction

$Z_i$  ionic charge

## Greek letters

$\Lambda_{12}, \Lambda_{21}$  - binary parameters of Wilson model

$\sigma_i$  - standard deviation of state variable

$\alpha, \beta$  - phase at equilibrium

$\mu$  - chemical potential

$\gamma$  - activity coefficient

$\phi$  - fugacity coefficient

$\theta_1, \theta_2$  - energy parameters

$\tau$  - parameter of NRTL-electrolyte model

$\rho$  - optimization variable

$\rho$  - closest approach parameter

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