Regression of NRTL Parameters from liquid–liquid equilibria for water + ethanol + solvent (dichloromethane, diethyl ether and chloroform) using particle swarm optimization and discussions at T =293.15 K

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Abstract

Experimental data taken from previous scientific studies of the liquid-liquid equilibrium (LLE) for ternary and quaternary systems {water +ethanol + dichloromethane (DCM), chloroform (CHCl3) or diethyl ether (DEE)} were correlated using the nonrandom two-liquid (NRTL) model. In Chemical Engineering, metaheuristic methods like the Genetic Algorithm (GA) and the Particle Swarm Optimization (PSO) are used to obtain binary interaction parameters for this model. In addition, the quality of the NRTL model predictions was assessed by calculating the variance of Root-Mean-Square Error (RMSE) between the experimental equilibrium and predicted data. As a result, the PSO RMSE values were better than the GA ones Therefore y, the PSO was the best optimization method for these systems.

Keywords: *Genetic Algorithm, Liquid-Liquid Extraction, Nonrandom Two-liquid model and Particle Swarm Optimization.*

I. Introduction

Liquid–liquid extraction (LLE) is a separation technique and is a fundamental mass transfer operation between two liquid phases which may be totally or partially miscible or immiscible. Typically water is the diluents. It is a polar compound and is generally a good solvent to extract polar compounds. The extraction process consists in extracting one or more constituents (solutes) from a solution by dissolution in an organic solvent where they are more soluble than in the initial liquid medium. Then the two obtained liquid phases are separated by decantation, achieving a solvent extraction process [1].

In fact a liquid-liquid extraction process requires three successive operations. First the two liquid phases are put into an intimate contact in special device (ampoules, columns, mixers) to encourage mass exchange [1]. The higher the extraction rates are, the greater the differences in solute concentration of the two phases in contact, and the larger the exchange surface between the two phases. Then a sufficient time is allowed to obtain equilibrium of the system, which is governed by the laws of diffusion and solubility such as partition coefficient of the solute from one phase to another. For the liquid-liquid system, the distribution coefficient (D) and separation factor (S) are fundamental and essential parameters that are always determined [1]. The distribution coefficient also known as the distribution ratio or partition coefficient is a quantitative factor which is used to assess the dispersion of the components dispersed in the equilibrium phase. Regarding the separation factor, it is used to assess the solvent extraction capacity [2, 3]. Finally, after their contact, under the effect of natural gravity (gravimetric) or decantation, a mechanical separation is performed between two liquid phases [4]. The densities of the two outgoing liquid phases are different. The solute rich phase is the extract whereas the solute poor phase is the raffinate (R) [4, 5]. The final concentration of the solute in each phase depends on its solubility in the involved liquids [1].

In liquid-liquid extraction (LLE), an activity coefficient thermodynamic model is required. Most of these models were developed from vapor-Liquid data and their application extended to liquid- liquid systems for phase equilibria predictions [6]. The usual procedure is based on the minimization of Gibbs free energy. The determination of the phase equilibria consists in solving the isoactivity equations along with the mass balance constraints [7]. In addition the required interaction parameters for the used model are obtained by minimizing a well defined objective function involving the system compositions [8]. Therefore one can see how important phase equilibrium calculations are in process modeling and simulation.

In fact thermodynamic modeling of liquid–liquid equilibria (LLE) is an important and difficult step in solvent extraction. One of the most significant issues is the estimation of the adjustable parameters required by the activity coefficient model. There are several activity coefficient models, such as NRTL (Non-Random Two-Liquids), UNIQUAC (UNIversal QUAsi Chemical) and UNIFAC (UNIversal Functional Activity Coefficient) [9].

Metaheuristic approaches have been used to calculate interaction parameters for vapor-Liquid [10] and liquid–liquid equilibrium [11] using these models. One of the the most used technique is based on the Genetic Algorithms (GA) and Particle Swarm Optimization (PSO) [12]

Consequently in this paper, the NRTL model, the GA and the PSO methods were a priori defined. Then, the proposed approach to solve the isoactivity equations was detailled. In addition, the GA and the PSO have been used to regress the parameters of the NRTL model in liquid-liquid equilibrium data for the ternary and quaternary presented in [13] using the minimization of solving the isoactivity equations following mass balance constraints.

II. Modeling of liquid-liquid equilibrium

A. NRTL model

Non-Random, Two-Liquids (NRTL) is an activity coefficient model, was proposed by Renon and Prausnitz in 1968 [14], based on Wilson's local composition theory [15] and Scott's two-liquid solution theory [16]. The activity coefficient (γ) expression for a binary system is shown as [17]:

$$\ln \gamma_i = \frac{\sum_{j=1}^{N} \tau_{ji}.G_{ji}.x_j}{\sum_{k=1}^{N} G_{ki}.x_k} + \sum_{j=1}^{N} \frac{x_j.G_{ij}}{\sum_{k=1}^{N} G_{kj}.x_k}\left(\tau_{ij} - \frac{\sum_{l=1}^{N} x_l.\tau_{lj}.G_{lj}}{\sum_{k=1}^{N} G_{kj}.x_k}\right) \tag{1}$$

With G_{ij} and τ_{ij} defined as follows [14, 17]:

$$\tau_{ij} = \frac{g_{ij}-g_{jj}}{R.T} = \frac{b_{ij}}{R.T} \tag{2}$$

$$G_{ij} = exp(\alpha_{ij}.\tau_{ij}) \tag{3}$$

Where:

g_{ij} is the energy interaction between i and j molecules,

α_{ij} is the non-randomness factor in the mixture, with $\alpha_{ij} = \alpha_{ji}$,

R is the universal gas constant in [$J{\cdot}mol^{-1}{\cdot}K^{-1}$],

T is the mixture temperature [K].

Three adjustable parameters αij , aij and aji of the NRTL model are calculated by regression of experimental equilibrium data for a specific system [18]. The parameters account simultaneously for mixed liquid interactions (gij and gji) and pure-component liquid interactions (gii and gjj). The non-randomness factor in the mixture (αij) varies from 0.2 to 0.47 [19] but for LLE systems is commonly set to a constant value of 0.2 [20].

B. Optimization methods:

The GA method was used to determine the interaction parameters of the NRTL model in [13, 21]. However in this study, the PSO method was used. In addition a comparative study was carried out when using the GA and the PSO methods for the interaction parameters determination.

B.1. Genetic algorithm (GA):

The genetic algorithm is an evolutionary optimizer (EO) [22], developed by John Holland and his collaborators in the 1960s and 1970s [14, 23]. It is a randomized search algorithm that was developed in an effort to simulate the mechanisms of natural selection and natural genetics or abstraction of biological evolution inspired by Charles Darwin's theory of natural selection. Genetic algorithms (GA) operate on string structures, like biological structures, which are evolving in time according to the rule of survival of the fittest by using a randomized and t structured information exchange by genetic operators (reproduction (mutation, crossover) and new gene selection) [22]. This notion can be applied for a search problem and select the set of best solutions (see Figure 1).

B.2. Particle Swarm Optimization (PSO):

Shi, Kennedy and Eberhart created the PSO algorithm [25, 26] for simulating social behavior [27]. It is a meta-heuristic intelligent optimization method for nonlinear functions by modeling the behavior of the biological swarms, such as fish swarm and bird flock looking for food and can search very large spaces of candidate solutions. PSO has been widely employed in many optimization issues due to its flexibility and ease of use. It has attracted significant research from a wide range of applications and has undergone several algorithm revisions and updates [28, 29].

The algorithm of PSO was simplified showed to be of an optimizing nature, as well reported in Kennedy and Eberhart book when they discussed philosophical elements and aspects of PSO and swarm intelligence [30]. Poli made an extensive survey of PSO applications [31, 32]. Bonyadi and Michalewicz recently released a comprehensive review on theoretical and experimental works on PSO [33].

By iteratively enhancing new solutions (particles) in the search space, the PSO enhances their positions, and the particle position vectors are considered candidate optimal solutions to the optimization issue. PSO can quickly explore the search space and converge to a global or local optimal solution by surfing in the search space of the optimization problem (see Figure 2). The following equations update the PSO algorithm's velocity and position vectors [30]:

$$v_i = \omega . v_i + c_1 . rand_1 . (p_{best} - x_i) + c_2 . rand_2 . (g_{best} - x_i) \tag{4}$$

$$x_i = x_i + k_{PSO} . v_i \tag{5}$$

Where:

v_i is the moving velocity of the particle,

x_i is the current location, ω is inertia weight,

c_1 and c_2 are positive acceleration factors,

$rand_1$ and $rand_2$ are the two random numbers distributed in the range of [0, 1],

k_{PSO} is the constriction factor,

p_{best} is the termed as personal best at the tth iterations, which refers to the best position found so far by the ith particle,

g_{best} is the termed as local best, which refers to the position found so far by the members in the ith particle's neighborhood that has the best fitness value.

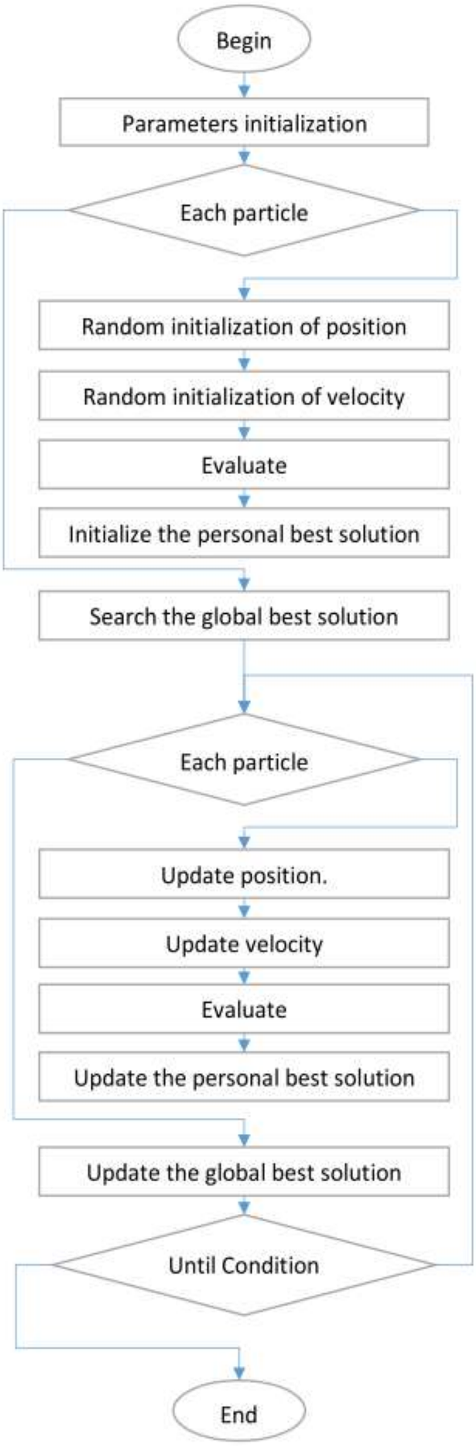

Figure 1: Flowchart of the genetic algorithm

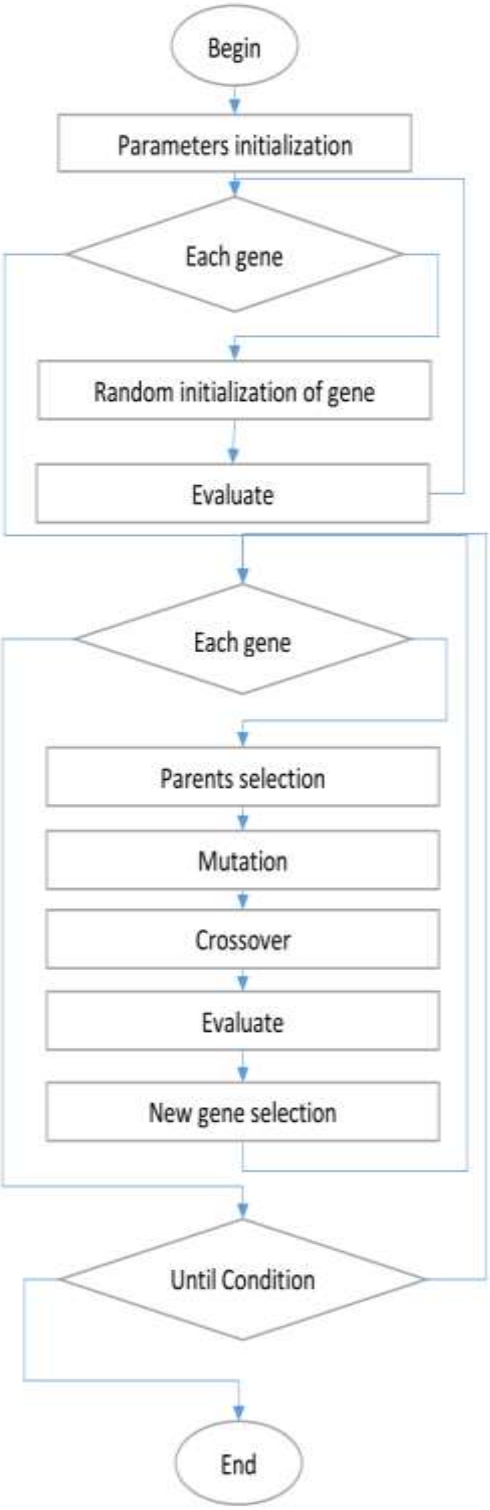

Figure 2. Flowchart of the particle swarm optimization algorithm

III. Equation solving isoactivity approach

In Equilibrium conditions between two phases or more, chemical potential allows to study of the phenomenon of diffusion of matter and to define the conditions of equilibrium phases. In the equilibrium condition in the case two phases, the chemical potential is equal that can be written as [8]:

$$\mu_i^{I} = \mu_i^{II} \quad (6)$$

Where:

μ_i^{I} , μ_i^{II} are the chemical potentials of component *i* , in phase *I* and *II* respectively.

Then, the Equation solving isoactivity approach utilizes uniformity of chemical potential of a component in all the phases. Fugacity defined from the chemical potential, which is the isothermal variation at constant composition of the chemical potential of a substance i pure or in mixture as a function of the pressure. The notion of fugacity allows in particular the calculation of phase equilibria that is given by the relation [34, 35]:

$$d\mu_i = R.T.\ d\ln f_i \quad (7)$$

Where:

μ_i is the chemical potential of a component *i*,

R is the universal gas constant (cal K^{-1} mol^{-1}),

T is the mixture liquid temperature (K),

f_i is the fugacity of é component *i*.

The fugacity is equal in two phases can be written as [8]:

$$f_i^{I} = f_i^{II} \quad (8)$$

Where:

f_i^{I} and f_i^{II} are the fugacities of component *i* , in phase *I* and *II* respectively.

The fugacity expression of a component i in phase can be written as [36]:

$$f_i^{\,I} = f_i^{Ri} .\gamma_i^{\,I} .\ x_i^{I} \quad (8.a)$$

$$f_i^{\,II} = f_i^{Ri} .\gamma_i^{\,II} .x_i^{II} \quad (8.b)$$

Where:

f_i^{Ri} is the fugacity of a component *i* in a real solution,

γ_i^{I} and γ_i^{II} are the activity coefficient of a component *i*, in phase *I* and *II* respectively,

x_i^{I} and x_i^{II} are the mole fraction of a component *i* in phase *I* and *II* respectively.

The activity coefficient is defined by the ratio between the real fugacity and the fugacity in an ideal solution that is given by the relation:

$$\gamma_i = f_i / f_i^{\,id} \quad (9)$$

Where:

γ_i is the activity coefficient of a component *i* ,

$f_i^{\,id}$ is the fugacity in an ideal solution.

Chemical activity is defined by the ratio of the real fugacity and in the standard state at the same temperature as the real state that is given by the relation [37]:

$$a_i = f_i \ / f_i^{\circ} \quad (10)$$

Where:

a_i is the chemical activity of component *i*

f_i° is the fugacity in the standard state of a component *i*.

In addition, chemical activity is could to define [8]:

$$a_i = x_i \ .\ \gamma_i \quad (11)$$

Therefore the equality of chemical potential can be replaced by equality of fugacities, which could be further more simplified to be the isoactivity equation as given in Eq. (12) [8]:

$$a_i^{I} = a_i^{II} \quad (12)$$

Where:

a_i^{I}, a_i^{II} are the chemical activities of component *i* in phase *I* and *II* respectively.

The equation (12) allows us to conclude that the equilibrium state of a system is reached only when the chemical potential of each of the constituents is identical in both phases. In this study, the equation (12) is the basis of all phase equilibrium calculations.

The isoactivity equations for LLE have been given in the equations (6)-(12), which take the following form in Equation (13) [38]:

$$x_i^{I}\ \gamma_i^{I} = x_i^{II}\ \gamma_i^{II} \quad (13)$$

The material balance must constrain these isoactivity equations, which can be calculated by entering the total amount of each component in the following equation [6]:

$$n_i^I + n_i^{II} = n_i \qquad (14)$$

Where:

n_i^I and n_i^{II} are the mole number of component *i* in phase *I* and *II* respectively,

n_i is the total amount of component *i* in the system.

Normalization of mole fraction requires two equations for equilibrium systems. Therefore the mass balance for a two-phase LLE system constraints can be written as [38]:

$$\sum_{i=1}^{N} x_i^I = 1 \qquad (15.a)$$

$$\sum_{i=1}^{N} x_i^{II} = 1 \qquad (15.b)$$

The isoactivity equations under mass balance constraints is the basic equations for both correlation and prediction of LLE system. For calculation of LLE systems present in [13, 21], the last mentioned operations are to be solved with a specified concentration of one component in one phase. With an initial estimation, a solution can be found by numerically solving the equations.

IV. Estimation of NRTL model interaction parameters

The parameter identification in local composition models is usually performed using LLE experimental data via the minimization of a suitable objective function. The objective function is defined in this study as following equation [39]:

$$minF = \sum_{k=1}^{m}\sum_{j=1}^{2}\sum_{i=1}^{c} w_{ik}^{j} \left(x_{ik}^{cal}(j) - x_{ik}^{exp}(j)\right)^2 \qquad (16)$$

Where:

m is the number of experimental tie-lines used in the correlation procedure,

x_{ik}^{cal} (j) and $x_{ik}^{exp}(j)$ are calculate and experimental the mole fractions respectively of component i at liquid phase j at tie line k,

w_{ik} is the weight associated with component i in phase j at tie line k, and in addition all the weights were set to one.

When employing the AG and the PSO approaches, the quality of the model NRTL predictions is evaluated by calculating the deviation of the RMSE between the experimental and predicted data, which is described as [6, 21]:

$$RMSE = \left[\frac{-F}{2.\,m.\,n}\right]^{0.5} \qquad (17)$$

Where:

m is the total number of tie lines,

n is the total number of components.

V. Correlation model and binary interaction parameters

The energy parameters (τ_{ij}) are searched in the range of [-15, 15] and all the non-randomness parameters (α_{ij}) equal 0.2. The metaheuristic methods was further tested by regressing the ternary and quaternary systems have presented in [13], the objective function in terms of mole fractions was minimized by 1000 iterations and using 200 particles, that are generated randomly, each particle is a group of six energy parameters of the NRTL model.

The determination of the binary interaction parameters and RMSE of the NRTL model using the PSO algorithm of MATLAB optimization toolbox in this present study, also these results were compared with literature results when using the GA algorithm, they were presented in [13], all the results are shown in tables 1, 2 and 3.

A. Separation of the mixture {Water + Ethanol} using mixed solvents (DEE + DCM): see Table 1

B. Separation of the mixture {Water + Ethanol} using mixed solvents (DEE +$CHCl_3$): see Table 2

C. Separation of the mixture {Water + Ethanol} using organic solvents (DEE, DCM or $CHCl_3$): see Table 3

Table 1. The NRTL binary interaction parameters and RMSE values for {water + ethanol + solvent (DEE, DCM or $CHCl_3$)} ternary system.

	Water + Ethanol + DEE			Water + Ethanol + DCM			Water + Ethanol +$CHCl_3$		
i-j	b_{ij}	b_{ji}	RMSE	b_{ij}	b_{ji}	RMSE	b_{ij}	b_{ji}	RMSE
Literature results [1]									
1-2	803.4	-494.7	1.9 %	3480.4	-522.9	1.58 %	-9.7331	2.2233	2.01 %
1-3	1553.7	618.9		2034.9	1750.9		6.018	4.7287	
2-3	-4.29.7	368.2		-200.5	3371		2.3244	-9.1458	
Results of the PSO method									
1-2	0.0352	3.5913	0.0112%	8.5366	1.9053	0.0161 %	10.3143	1.8460	0.0137%
1-3	6.1661	4.7208		4.2771	4.4592		-8.4507	5.9755	
2-3	3.1735	15		1.9498	7.6684		-13.5031	2.8034	

Table 2. The NRTL binary interaction parameters and RMSE values of quaternary systems {Water + Ethanol + Mixed solvent ($CHCl_3$ + DEE)}.

Water + Ethanol + mixed solvents (..% DCM + ..%DEE)									
	+25% DCM +75%DEE			+50% DCM +50%DEE			+75% DCM +25%DEE		
i-j	b_{ij}	b_{ji}	RMSE	b_{ij}	b_{ji}	RMSE	b_{ij}	b_{ji}	RMSE
Literature results [1]									
1-2	-195.7	-624	1.09 %	2786.2	-536.7	1.01%	3242.9	-456.2	1.04%
1-3	1606.7	1529.7		1580.2	2197.1		1909.7	2108.7	
2-3	-535.4	-457		-156.5	2571.9		-152.4	3305.2	
Results of the PSO method									
1-2	15	15	0.0181%	4.70.68	10.1229	0.0324 %	15	3.7369	0.0214 %
1-3	-10.7364	0.7642		3.0007	4.6614		6.8511	4.2202	
2-3	-15	3.0295		10.6621	4.5641		2.133	8.0408	

Table 3. The NRTL binary interaction parameters and RMSE values of quaternary systems {Water + Ethanol + Mixed solvent ($CHCl_3$ + DEE)}.

	Water + Ethanol + mixed solvents (..%$CHCl_3$ +..%DEE)								
	+ (25%$CHCl_3$ +75%DEE)			+ (50%$CHCl_3$ + 50%DEE)			+ (75%$CHCl_3$ +25%DEE)		
i-j	b_{ij}	b_{ji}	RMSE	b_{ij}	b_{ji}	RMSE	b_{ij}	b_{ji}	RMSE
	Literature results [1]								
1-2	3501.5	106	1.69 %	3729.8	-339.9	1.55 %	2661.8	-439.4	1.23 %
1-3	1807.2	196.7		2804	1274.1		1499.7	929.8	
2-3	94.5	1224.4		-297.7	2432.2		-56.7	2562.1	
Results of the PSO method									
1-2	15	15	0.0361 %	15	4.5306	0.0575 %	10.8656	3.7098	0.0085 %
1-3	-9.7999	14.165		7.9338	3.9851		9.4421	5.5779	
2-3	-15	2.9384		2.5301	8.3620		6.2931	1.6828	

VI. Results and discussion

In **ternary system**, the smallest RMSE value was 1.58 for individual solvent DCM and 0.0112 for individual solvent DEE when using the GA method and the PSO method respectively.

In **quaternary system**, the smallest RMSE value was 1.01 for mixed solvent (50% DCM +50%DEE), and 1.23 for mixed solvent (75%CHCl3 +25%DEE) when using the GA method, but when using the PSO method, the value of RMSE was 0.0181 for mixed solvent (25% DCM +75%DEE) and 0.0085 for mixed solvent (75%CHCl3 + 75%DEE).

Finally, in the liquid-liquid equilibrium (LLE) for ternary and quaternary systems {water +ethanol + dichloromethane (DCM), chloroform (CHCl3) or diethyl ether (DEE)}, the RMSE values of the PSO method are smaller than the RMSE values of the GA method. Therefore, the best method is PSO. In addition, the best individual solvent is DEE in ternary system, and the best-mixed solvent is (25% DCM +75%DEE) and (75%CHCl3 +25%DEE) in quaternary system, because they have had the lowest RMSE values.

VII. Conclusion

In this study, the PSO and the GA are optimization methods and the minimization by the objective function have been used to determine the interaction parameters of NRTL model in the liquid-liquid equilibrium data of the ternary and quaternary chemical systems have presented in [13].

The RMSE of PSO is smaller than the RMSE corresponding to the GA results. Therefore, PSO method is more successful in the determination of the NRTL parameters for liquid–liquid equilibria data of the considered systems in [13].

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List of Symbols

LLE	Liquid-Liquid Equilibrium
PSO	Particle Swarm Optimization
NRTL	Nonrandom Two-Liquid
RMSE	Root-Mean-Square Error
D	Distribution coefficient
S	Separation factor
T	Temperature of mixture [K]
R	Universal gas constant [J·mol–1·K–1]
G	Energy interaction
a	Activity
α	Non-randomness factor in the mixture
τ	Energy parameters
γ	Activity coefficient
v_i	Moving velocity of the particle
x_i	Current location
ω	Inertia weight
c_1 , c_2	Positive acceleration factors
$rand_1$, $rand_2$	Two random numbers distributed in the range of [0, 1]
$\boldsymbol{k_{PSO}}$	Constriction factor
p_{best}	Personal best
g_{best}	Local best
μ_i^{I} , μ_i^{II}	Chemical potentials of component *i*, in phase *I* and *II* respectively.
μ	Chemical potential
f_i	Fugacity
f_i^{I}, f_i^{II}	Fugacities of component *i* , in phase *I* and *II* respectively.

f_i^{Ri}	Fugacity of a component *i* in a real solution,
$\gamma_i^I, \gamma_i^{II}$	the activity coefficient of a component *i*, in phase *I* and *II* respectively,
x_i^I , x_i^{II}	Mole fraction of a component *i*, in phase *I* and *II* respectively.
f_i°	Fugacity in the standard state of a component *i*.
a_i^I, a_i^{II}	Activities of component *i*, in phase *I* and *II* respectively .
n_i^I and n_i^{II}	Mole number of component *i* , in phase *I* and *II* respectively,
n_i	Total amount of component *i* , in the system.
w_{ik}	Weight associated with component i in phase j at tie line k,
m	Number of experimental tie-lines used in the correlation procedure,
n	Number of components
x_{ik}^{cal} (*j*)	Calculate mole fractions of components
$x_{ik}^{exp}(j)$	Experimental mole fractions of components
i	Component
j	Liquid Phase
k	Number of tie lines

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