

Interaction parameters for ternary and quaternary liquid systems using particle swarm optimization

Sabrina Hebboul¹; Mourad Korichi¹; Amel Hebboul²

¹: Department of Process Engineering, Dynamics, Interaction and Reactivity of Systems laboratory, University of Kasdi Merbah, Ouargla, Algeria, sabrinahebboul30@gmail.com

²: Department of Mathematics and Computer science, High Normal School Assia Djébar, Ali Mendjli, Automatic and Robotic Laboratory, University of Frères Mentouri, Constantine, Algeria, ahebboul@yahoo.fr

Received: 08/03/2022

Accepted: 20/06/2022

Published online: 17 /07/2022

Abstract

In liquid-liquid equilibrium (ELL) calculations several thermodynamic models may be used for the calculation of the activity coefficient. In the present study the NRTL (Nonrandom Two-Liquids) was used. It is based on the concept of local composition and it requires binary interaction parameters which are calculated from experimental data by minimizing an objective function expressed either in terms of activities or mole fractions. The used minimization technique was the stochastic optimization method, known as the Particle Swarm Optimization. The considered ternary and quaternary systems were Water as diluent, Ethanol as the solute and Dichloromethane, Chloroform and Diethyl ether as solvents, considered individually or as binary mixtures. The obtained results were assessed by comparison with the experimental values, by calculating the Root-Mean-Square Error. This showed that the nature of the objective function did influence the agreement with the experimental values with the hybrid (PSO-), leading to the best accuracy and with diethyl ether and 50% dichloromethane (DCM) +50% diethyl ether (DEE) in the ternary and quaternary systems, as the best individual and -mixed solvents, respectively.

Keywords: Nonrandom Two-Liquid model, Objective Function, Particle Swarm Optimization and Thermodynamic systems.

I. Introduction

Liquid-liquid extraction known also as solvent extraction is a separation technique used to separate constituents from liquid mixtures, particularly when their volatilities are close, giving azeotropes or are easily thermo-degradable [1]. It is a fundamental mass transfer operation between two liquid phases totally or partially miscible or immiscible. It consists of extracting one or more solutes from a solution (liquid mixture) by dissolution in a solvent (individual or mixed). Provided a sufficient contact time is allowed, the liquid-liquid equilibrium of the system is obtained with two distinct phases that can be separated by a simple decantation [1]. The considered systems can be binary, ternary, quaternary, etc depending on the number of the constituents [2, 3].

Many recent research works have focused on liquid-liquid equilibrium (LLE) difficulties such as phase equilibrium calculations, chemical equilibrium calculations, binary interaction parameter identification of thermodynamic models, phase stability analysis, and other fluid characterization problems [4].

Liquid phases in equilibrium can be modeled using thermodynamic models such as NRTL (Non-Random, Two-Liquids) model and its expansions. However the use of these thermodynamic models depends on the availability of interaction parameters which should be appropriately regressed from experimental data [5].

Recently several optimization methods have been used to simulate and calculate liquid-liquid equilibrium [6] and one can cite: Simulated Annealing (SA), Simulated Genetic Algorithms

(GA), Tabu Search (TS) method, Harmony Search (HS) method, Ant Colony Optimization (ACO), Random Tunneling (RT) method, Differential Evolution (DE) method and Particle Swarm Optimization (PSO) [4, 7, 8].

The NRTL parameters were effectively regressed from liquid-liquid equilibria data using the PSO method, a global optimization algorithm [5].

In this paper, the PSO method was used to regress the adjustable parameters of the NRTL model for ternary and quaternary liquid-liquid systems reported in [9]. In general, there are two methods for calculating the LLE, such as the Gibbs energy minimization or solving the isoactivity equations (the K-value method) and for determining the phase behavior of LLE systems [10]. But in this paper, solving the isoactivity equations was used due to its simplicity compared to the Gibbs free energy minimization [11].

II. Liquid-liquid equilibrium conditions

In chemical thermodynamics, the phase equilibrium condition between two phases I and II for any constituent *i* of the liquid-liquid mixture, is given by the equality of the temperatures T, pressures P and chemical potentials μ of the constituents in each phase, and the system of equations can be written [12–15] as:

$$T^I = T^{II} \tag{1}$$

$$P^I = P^{II} \tag{2}$$

$$\mu_i^I = \mu_i^{II} \tag{3}$$

Where:

T^I and T^{II} are the temperature of the phase *I* and *II* respectively;

P^I and P^{II} are the pressures of the phase *I* and *II* respectively;

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

The chemical potential can be considered as the driving force during mass transfer that results in phase equilibrium.

For a same reference state the chemical potential is related to activity as [16]:

$$\mu_i^I = R.T. \ln a_i^I \tag{4}$$

$$\mu_i^{II} = R.T. \ln a_i^{II} \tag{5}$$

From the systems of equation (3)-(5), the activities of each constituent in each phase are equal and the equilibrium condition (3) becomes [13, 17]:

$$a_i^I = a_i^{II} \tag{6}$$

Where:

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

The equation (6) 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 the two phases. In our work, the system of equations (6) is the basis of all equilibrium calculations between phases.

The fugacity is equal in the two phases at equilibrium leading to a the following system of equations [12]:

$$f_i^I = f_i^{II} \tag{7}$$

Where:

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

In addition, the fugacity expression of a component *i* in phase can be written as [2]:

$$f_i^I = f_i^{Ri} . x_i^I . \gamma_i^I \tag{8}$$

$$f_i^{II} = f_i^{Ri} . x_i^{II} . \gamma_i^{II} \tag{9}$$

Where:

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

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

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

If the same reference state is considered , Equations (7)-(9) equations take the following forms [5, 18–21]:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \tag{10}$$

The material balance must constrain these isoactivity equations, which can be calculated by entering the total amount of each component in the following equation [5, 11]:

$$n_i^I + n_i^{II} = n_i \tag{11}$$

Where:

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

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

The mole fraction normalization requires two equations for any equilibrium systems. Therefore the mass balance for a two-phase LLE system constraints can be written as [6, 18, 19, 21]:

$$\sum_{i=1}^N x_i^I = 1 \tag{12}$$

$$\sum_{i=1}^N x_i^{II} = 1 \tag{13}$$

Finally, the Equation solving isoactivity approach utilizes uniformity of chemical potential of a component in all the phases. Therefore, the isoactivity equations for phase equilibrium are (3)-(13). The isoactivity equations under mass balance constraints are the basic equations for both correlation and prediction of the LLE system. For the calculation of LLE systems reported in [9, 22], the last mentioned operations was to solve with a specified concentration of one component in one phase. With an initial estimation, a solution can be found by numerically solving the equations. The activity coefficient can be calculated by solving the Gibbs excess free energy equation. The latter is determined by a thermodynamic model such as NRTL, UNIQUAC and UNIFAC [9].

III. Regression of NRTL parameters using PSO

A. NRTL

The thermodynamic model was used in this paper is the Nonrandom Two-Liquid (NRTL) model as an activity coefficient (γ) model for calculating phase equilibria [23, 24]. This model accurately represents VLE and LLE systems that are significantly non-ideal [14]. The activity coefficient (γ) expression for a binary system is shown [11, 18–21, 23, 25, 26]

$$\ln \gamma_i = \frac{\sum_{j=1}^N \tau_{ji} \cdot G_{ji} \cdot x_j}{\sum_{k=1}^N G_{ki} \cdot x_k} + \sum_{j=1}^N \frac{x_j \cdot G_{ij}}{\sum_{k=1}^N G_{kj} \cdot x_k} \left(\tau_{ij} - \frac{\sum_{l=1}^N x_l \cdot \tau_{lj} \cdot G_{lj}}{\sum_{k=1}^N G_{kj} \cdot x_k} \right) \tag{14}$$

With G_{ij} and τ_{ij} defined as follows [18–20, 23, 27]:

$$G_{ij} = \exp(\alpha_{ij} \cdot \tau_{ij}) \tag{15}$$

$$\tau_{ij} = \frac{A_{ij}}{R \cdot T} \tag{16}$$

Where:

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

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

R is the universal gas constant in $\text{cal K}^{-1} \text{mol}^{-1}$,

T is the mixture temperature in K.

The NRTL model has three adjustable parameters specific to a particular pair of molecules, two adjustable energy parameters (τ_{ij} and τ_{ji} or A_{ij} and A_{ji} and one non-randomness parameter ($\alpha_{ij} = \alpha_{ji}$), are independent of composition and temperature, and are determined through regression of experimental data for a specific system [5, 24]. The non-randomness parameter in the mixture (α_{ij}) varies from 0.2 to 0.47 [14] and is usually set at a constant value of 0.2 for LLE systems [28]. This model is frequently used to simulate and compare data that is able to correlate vapour-liquid equilibria [28, 29] and liquid-liquid equilibria systems [21, 29, 31, 32] with reasonable accuracy and can predict equilibria of ternary systems from binary data, including highly non-ideal mixes, particularly partially immiscible systems. Furthermore, the LLE of quaternary systems has been accurately predicted using parameters fitted from ternary LLE data [33, 34].

B. Particle Swarm Optimization Algorithm

Since Kennedy and Eberhart first created the particle cluster optimization algorithm in 1995 [19, 35, 36], it has drawn much attention and investigation from many researchers [37]. Particle swarm optimization is a population-based evolutionary method with ideological sources in artificial life theory and evolutionary computing [38].

The term "particle swarm optimization" comes from the study of birds foraging behavior, in which a group of birds searches for food at random. If there is only one piece of food in this area, the most straightforward and efficient search approach is to look for food in the closest location to the food. Recently, this model was used to address optimization problems. [39, 40].

The PSO [41] is a computational approach for optimizing a problem by iteratively trying to develop a candidate solution in terms of a given quality measure in computational science. It solves a problem by generating a population of candidate solutions, which are referred to as particles, and moving them around in the search space using a simple mathematical formula based on their position and velocity. The movement of each particle is influenced by its local best-known location, but it is also guided toward the best-known positions in the search space, which are modified as better positions are discovered by other particles. The swarm is supposed to shift toward the best solutions as a result of this.

The PSO is a problem-solving algorithm based on a population of individuals, or particles, where each particle is considered a solution to the problem. During displacement, each particle's location is altered based on its best-produced position as well as the global position based on its neighbors [36].

The particle has a suitable value determined by the objective function in addition to its position and velocity. Each particle remembers and follows the current ideal particle while it explores the solution space: each search (iteration) includes some random factors, but they are not fully random. If a better solution is identified, this can be used to find the next best solution. Particle swarm optimization, in particular, begins with a random beginning particle [42].

The particle changes its position in each iteration by tracking two "extreme points": one is the particle's best solution (i.e., individual extreme point, p_{best}), and the other is the extreme point (g_{best}) of the entire particle swarm or the entire neighborhood (l_{best}). Particles modify their flight direction and speed based on the original inertia to preserve the overall optimum [43, 44].

In the PSO, the position vectors of the particles are the candidate optimal solutions to the optimization problem. By flying in the search space of the optimization problem, the PSO can accomplish the fast exploration of the search space and converge to a global/local optimal solution. The velocity and position vectors of the PSO algorithm are updated by equations (17) and (18) [45]. Therefore, the mathematical description of the origin PSO method is as follows [36, 46, 47]:

$$v_i = \omega * v_i + C_1 * r_1 * (p_{best} - x_i) + C_2 * r_2 * (g_{best} - x_i) \quad (17)$$

$$x_i = x_i + k_{PSO} * v_i \quad (18)$$

Where:

v_i is the velocity of the particle i , x_i is the current position, ω is inertia weight, k_{PSO} is constriction factor, r_1 and r_2 are two random numbers distributed in the interval $[0, 1]$, C_1 and C_2 are positive or nonnegative acceleration constants; also known as convergence factors.

The convergence factor C_1 is called cognitive constant, which represents the characteristics of particles learning from their own optimal state. These two parameters represent the acceleration weights of particles approaching individual and global extrema, respectively. The size of C_1 determines the cognitive ability of particles, that is, the ability of particles to learn from themselves. The size of C_2 determines the social information sharing ability of particles, that is, the ability of particles to advance toward the current global optimal value [42],

p_{best} is the best personal position at the t^{th} iterations, which refers to the best solution found so far by the i^{th} particle, g_{best} is the global best position, which refers to the global best solution found so far by the swarm in the i^{th} particle's neighbourhood that has the best objective function value.

It can be seen from the velocity update equation (17) that the first flying speed of a particle is mainly determined by the following three components [42]. The previous velocity is the first part that is the speed of the particle at time t , which represents the particle's trust in the flight speed at time t and makes inertial motion according to its velocity at time t . The cognitive part of the particle itself is the second part, which represents the particle's thinking about its position, thinking about the position before the particle itself, to determine the next step. The cognitive part indicates that a particle learns from its searching experience. The social part of particles is the third part, which represents the information exchange and cooperation between particles and their peers. The social part indicates that a particle can learn from other particles or learn from the global best solution. In the process of searching, particles synthesize their previous flight experience and the experience of their companions and finally determine their own flight speed according to the formula (17). The position particle

was updated in the search space at each iteration using equation (18).

B.1. PSO Algorithm Description

The PSO algorithm can be explained as the following six main steps [36, 42]:

1- Initialization: The essential parameters of the method, as well as the position and velocity of all particles (population size n), are randomly initialized in this process.

2- Evaluation of the initial population: The initial fitness value of each particle in the population is determined, and using the initial position of each particle as an individual extremum, the optimal position of the current population is obtained. The particle with the highest fitness is chosen as the global best particle ' g_{best} '.

3- Updating position and velocity: Update the position and the velocity of each particle according to two equations previously mentioned (4) and (5).

4- Evaluation of the updated population: this is based on the comparison of the current fitness and the previous best values. If the current fitness value is higher than the previous best value, the particle's previous best value is changed to the current fitness value, and its position is updated ' p_{best} '.

5-Check to see if the terminal condition is met: If the current fitness value is better than the previous population best value, the previous population best value is set as the current fitness value to update the global best solution of the population.

6- Output results and check the end conditions: In this step is output when the best solution is obtained "gbest" during the optimization process and the iteration is terminated. If the optimization results meet the conditions for the iteration stops. Otherwise, go back to step 4 and continue the optimization until the iteration stop condition is met.

C. Estimation of NRTL model's parameter by objective functions suitable

The binary interaction parameters for the NRTL model were estimated from the experimental equilibrium LLE data [48] by minimizing a suitable objective function with constrained minimization using the PSO method (bacha et al). There are two types of objective functions that are usually used to

regress the parameters, including objective functions in terms of activities and objective functions in terms of mole fractions (concentrations) [12], the objective functions were the sum of the square of the error between the experimental and calculated compositions of all the components over the entire set of tie lines, which are given by:

C.1. Objective functions in terms of activities (OF_a) [12, 49]:

$$OF_a = \sum_{i=1}^3 \sum_{k=1}^M (x_{ik}^I \cdot \gamma_{ik}^I - x_{ik}^{II} \cdot \gamma_{ik}^{II})^2 \quad (19)$$

Where:

x_{ik}^I and x_{ik}^{II} are the mole fraction of component i in phase I and II at tie line k respectively.

γ_{ik}^I and γ_{ik}^{II} are the activity coefficient of component i in phase I and II at tie line k respectively.

The activity coefficients calculated are dependent on the experimental mole fractions and parameters of a thermodynamic model [12].

C.2. Objective functions in terms of mole fractions (OF_x) [12, 27, 50, 51]:

$$OF_x = \sum_{i=1}^3 \sum_{j=1}^2 \sum_{k=1}^M (x_{ik}^j_{cal} - x_{ik}^j_{exp})^2 \quad (20)$$

Where:

$x_{ik}^j_{cal}$ and $x_{ik}^j_{exp}$ are the experimental and calculated mole fraction of component i in phase j at tie line k , respectively.

The parameters of a thermodynamic model have an impact on the calculated mole fractions [12].

In this study, for the convenience of evaluating the quality of correlation in case using the PSO method, two methods were applied: a hybrid (PSO- OF_a) and a hybrid (PSO- OF_x) methods. In addition, the goodness of the model predictions was judged by calculating the variance or Root Mean Square Error (RMSE), which is used to determine the accuracy of the fit between the experimental and predicted data by the NRTL model, the following equation of RMSE is defined as [22, 47, 51, 52]:

$$RMSE = \sqrt{\frac{F}{N_p + N_b + N_c}} \quad (21)$$

Where: F is the objective functions in terms of activities when using the hybrid (PSO- OF_a) method or the objective functions in terms of mole fractions

when using the hybrid (PSO- OF_x) method, N_p , N_b and N_c , Number of phases, Number of conodals and Number of constituents respectively.

D. Binary interaction parameters and RMSE values

Determining the interaction parameters is the most difficult, and it necessitates the use of extremely rigorous optimization approaches that can yield relatively accurate outcomes. Therefore, in the framework of this study, the PSO method is used as an optimization technique.

To predict the LLE data using a specific thermodynamic activity model, the experimental tie-line data for ternary and quaternary systems previously mentioned were correlated using the NRTL model at $T=293.15$ K and 1 atm [9].

Firstly, all the non-randomness parameters (α_{ij}) are fixed as 0.2 [49] and the energy parameters (τ_{ij} and τ_{ji}) are searched in the range of [-15, 15].

In addition, the positive acceleration constants $C_1=1.49445$ and $C_1 = C_2$ [5]. Then, the objective function was minimized using 200 particles that are generated randomly, each particle is a group of six energy parameters of the NRTL model. The optimization method was further tested by regressing ternary and quaternary LLE systems and 1000 iterations in all these systems.

All of the correlating results show good agreements with the experimental data for the chemical systems. The low values of root mean square error (RMSE) confirm the ability of the NRTL model to predict the given experimental data. The NRTL

model's binary interaction parameters were estimated from the experimental data with minimizing by two suitable objective functions for the liquid-liquid equilibrium of the systems studied with constrained minimization using the PSO algorithm of MATLAB optimization toolbox.

IV. Results and discussion

The binary interaction parameters and RMSE values have been showing in Tables 1 and 2.

First, the distribution coefficient (D) and the separation factor (S) were calculated for the quaternary systems and were presented in [9]. Then, the distribution coefficient is used to evaluate the distributed components in the equilibrium phase and the separation factor is used to evaluate the solvent extraction ability. Therefore, these parameters are necessary and very important to determine the factors influencing the liquid-liquid extraction such as the properties of the solvent and the solute, the temperature of the extraction [1].

The extraction capacity of the mixed solvents calculated by the distribution coefficients and the separation factor showed that the system of mixture solvent (50% DCM+ 50% DEE) had a higher separation factor when compared to others systems {Water +Ethanol+ mixed solvent (25% DCM+ 75% DEE) or (75% DCM+ 25% DEE)}

On the other hand, the mixed solvent (50% $CHCl_3$ + 50% DEE) was the best in terms of distribution coefficient and separation factor when comparing with other systems {Water + ethanol + mixture solvent (25% $CHCl_3$ + 75% DEE) or (75% CH_3Cl + 25% DEE)} [9].

Table 1. NRTL binary interaction parameters and RMSE values for ternary systems {Water + Ethanol} using individual organic solvents (DEE, DCM or $CHCl_3$)

i-j	Water + Ethanol + DEE			Water + Ethanol + DCM			Water + Ethanol + $CHCl_3$		
	A_{ij}	A_{ji}	RMSE	A_{ij}	A_{ji}	RMSE	A_{ij}	A_{ji}	RMSE
The hybrid (PSO- OF_q)									
1-2	7.7473	6.5152	0.1692%	2.6475	2.134	0.0963%	0.9347	2.5185	0.0249%
1-3	3.4246	3.2551		4.5338	6.4604		6.1405	5.0296	
2-3	1.0404	8.9014		2.5433	2.4544		2.3008	1.6437	
The hybrid (PSO- OF_x)									
1-2	0.0352	3.5913	0.0112%	8.5366	1.9053	0.0161%	10.3143	1.846	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. NRTL binary interaction parameters and RMSE values for quaternary systems {Water + Ethanol} using mixed solvents (DEE + DCM) or (DEE + CHCl₃)

Water + Ethanol+ mixture solvent (50% DCM +50%DEE) or (50%CHCl ₃ +50%DEE)						
Water + Ethanol+ (50% DCM +50%DEE)				Water + Ethanol+ (50%CHCl ₃ + 50%DEE)		
i-j	A _{ij}	A _{ji}	RMSE	A _{ij}	A _{ji}	RMSE
The hybrid (PSO-OF _a)						
1-2	2.5218	2.6097	0.072%	0.4117	2.6080	0.1282 %
1-3	4.4875	6.7426		3.9536	7.2047	
2-3	2.5931	2.6208		6.4331	2.4984	
The hybrid (PSO-OF _x)						
1-2	4.70.68	10.1229	0.0324 %	15	4.5306	0.0575 %
1-3	3.0007	4.6614		7.9338	3.9851	
2-3	10.6621	4.5641		2.5301	8.3620	

A. Analysis of the results for ternary and quaternary system:

From the table 1 and the table 2, the values of RMSE were obtained less than 0.1692 and 0.1282 for the individual solvent DEE and for the mixture solvent {**Water + Ethanol + (50% CHCl₃ + 50% DEE)**} respectively, when using the hybrid (PSO-OF_a) method.

Therefore, the results were compared in order to choose the best method and to find the best solvent for the considered liquid-liquid extractions with respect to the ternary and the quaternary systems previously mentioned. The best results were obtained when using the hybrid (PSO-OF_x) method rather than the hybrid (PSO-OF_a) and this according to low values of RMSE which were 0.0112%, 0.0161 % and 0.0137% for individual solvent **DEE**, **DCM** and **CHCl₃** respectively and 0.0324 and 0.0575 % for the mixture solvent (**50% DCM +50%DEE**) and the mixture solvent (**50%CHCl₃ + 50%DEE**), respectively.

In addition the lowest value of RMSE was obtained when using individual solvent **DEE**, therefore it was the best individual solvent and the lowest value of RMSE is when using mixture solvent (**50% DCM +50%DEE**), therefore it was the best mixed solvent.

Finally, the RMSE results demonstrate that the thermodynamic model NRTL was able to represent better the liquid-liquid equilibrium [49] in the presence of individual or mixed solvents using the hybrid (PSO-OF_a) and the hybrid (PSO-OF_x) methods.

V. Conclusion

The liquid-liquid equilibria of the ternary and quaternary systems that have been used and are Water + ethanol + solvent (DCM, DEE or CHCl₃) is the ternary systems, {Water + Ethanol + mixed solvent (50% CHCl₃ + 50% DEE) or (50% DCM +

50%DEE)} are the quaternary systems. All these systems were presented in [9]. In this research, the hybrid (PSO-OF_a) and the hybrid (PSO-OF_x) methods have been used to regress the interaction parameters of the NRTL model for the systems previously mentioned.

In addition, the approach solving isoactivity equations was used to determine the phase behavior of LLE systems and for calculating the LLE.

Then, the parameter identification is performed using LLE experimental data via the minimization of a suitable objective function. Besides, it is essential to note deeply and focus that the selection of the objective function used for the parameter identification influences both prediction and correlation results of NRTL models [25]. In this study, current functions were used: the objective function in term of activity (OF_a) or the objective function in term of mole fraction (concentration) (OF_x).

Finally, the results were compared, to select the best method and the best solvent for liquid-liquid equilibria data. As the Root-Mean-Square Error (RMSE) was calculated to determine the accuracy of the fit between experimental equilibrium data and calculate data predicted by the NRTL model. Therefore, the results show that the hybrid (PSO-OF_x) method performs better in the accuracy of the fit than the hybrid (PSO-OF_a) method. As a result, objective functions expressed in terms of LLE concentrations (i.e. experimental tie-lines) are better for parameter identification in thermodynamic models. For the LLE data modeling, the next objective function was employed based on these facts [25]. In addition, the best solvent is DEE for ternary system and the best mixed solvent is (50% DCM +50%DEE) for quaternary system.

Acknowledgments

First, we would like to thank ALLAH who helps us to do this scientific research paper.

In addition, we want to thank the Department of Processes Engineering, Faculty of Applied Sciences, Kasdi Merbah University, Ouargla, Algeria.

Nomenclature and units

LLE	Liquid-Liquid Equilibrium
PSO	Particle Swarm Optimization
NRTL	Nonrandom Two-Liquid
OF_x	Objective functions in terms of mole fractions
OF_a	Objective functions in terms of activities
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 and C_2	Positive acceleration factors
r_1 and r_2	Two random numbers distributed in the range of [0, 1]
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	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.
a_i^I, a_i^{II}	Activities of component i, in phase I and II respectively.
n_i^I, 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}^j cal	Calculate mole fractions
x_{ik}^j exp	Experimental mole fractions
x_{ik}^I	Mole fraction in phase I
x_{ik}^{II}	Mole fraction i in phase II
i	Component
j	Liquid Phase
k	Number of tie lines

References:

[1] S. Hebboul and M. Korichi, "Extraction liquide-liquide: types, facteur influençant," *Algerian Journal of Engineering Architecture and Urbanism*, vol. 5, no. 5, pp. 390–403, 2021.

[2] H. Baker, "Alloy phase diagrams, ASM handbook," *ASM International (The Materials Information Society), USA*, 1992.

[3] H. Baker, "Section 1 Introduction to alloy phase diagrams," 1992.

- [4] K. Merzougui, A. Hasseine, S. Regab, and D. Laiadi, "Hybridization of Cuckoo Search and Firefly Algorithms to Calculate the Interaction Parameters in Phase Equilibrium Modeling Problems," *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, vol. 39, no. 3, pp. 271–285, 2020.
- [5] Zheng Li, "Thermodynamic Modelling of Liquid–liquid Equilibria Using the Nonrandom Two-Liquid Model and Its Applications," 2015.
- [6] A. Merzougui, A. Hasseine, and D. Laiadi, "Application of the harmony search algorithm to calculate the interaction parameters in liquid–liquid phase equilibrium modeling," *Fluid phase equilibria*, vol. 324, pp. 94–101, 2012.
- [7] Z. Haibo, "New strategies for global optimization of chemical engineering applications by differential evolution," 2012.
- [8] M. Panda, "Performance comparison of genetic algorithm, particle swarm optimization and simulated annealing applied to TSP," *International Journal of Applied Engineering Research*, vol. 13, no. 9, pp. 6808–6816, 2018.
- [9] O. Bacha, "Experimentale et modelisation des equilibres liquide-liquide des systemes ternaires et quaternaires," Biskra, 2016.
- [10] S. I. Sandler, "Chemical, biochemical, and engineering thermodynamics," 2006.
- [11] Z. Li, K. A. Mumford, K. H. Smith, J. Chen, Y. Wang, and G. W. Stevens, "Solution Structure of Isoactivity Equations for Liquid–Liquid Equilibrium Calculations Using the Nonrandom Two-Liquid Model," *Industrial & Engineering Chemistry Research*, vol. 55, no. 10, Mar. 2016, doi: 10.1021/acs.iecr.5b04469.
- [12] J. M. Sørensen, T. Magnussen, P. Rasmussen, and A. Fredenslund, "Liquid–liquid equilibrium data: Their retrieval, correlation and prediction Part II: Correlation," *Fluid Phase Equilibria*, vol. 3, no. 1, pp. 47–82, 1979.
- [13] Boulouf Ayache, "Application d'algorithmes évolutionnistes avec hybridation aux calculs des équilibres liquide-liquide dans les systèmes ternaires," Ouargla, 2017.
- [14] J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular thermodynamics of fluid-phase equilibria*. Pearson Education, 1998.
- [15] Tester Jefferson W. and Modell Michael, *Thermodynamics and Its Applications, 3rd edition*, Prentice Hall PTR. Cambridge, Massachusetts: Pearson, 1996.
- [16] D. v. Malakhov, "A linkage between the activity and the chemical potential," *Canadian Metallurgical Quarterly*, vol. 59, no. 1, Jan. 2020, doi: 10.1080/00084433.2019.1630213.
- [17] C.-C. Chen, "A segment-based local composition model for the gibbs energy of polymer solutions," *Fluid Phase Equilibria*, vol. 83, Feb. 1993, doi: 10.1016/0378-3812(93)87033-W.
- [18] S. Regabe, A. Merzougui, A. Hasseine, D. Laiadi, and H. Bouredji, "Experimental Data and Modeling of Salt Effect on Liquid-Liquid Equilibrium of the Ternary (Water+ 1-Propanol+ Hexane) System at 298K," *Iran. J. Chem. Chem. Eng. Research Article Vol*, vol. 39, no. 6, 2020.
- [19] H. Binous, K. Mejbri, and A. Bellagi, "Application of graduate-level numerical tools to teach phase equilibria of liquid ternary systems," *Computer Applications in Engineering Education*, 2021.
- [20] H. Binous and A. Bellagi, "Calculation of ternary liquid-liquid equilibrium data using arc-length continuation," *Engineering Reports*, vol. 3, no. 2, p. e12296, 2021.
- [21] Z. Li *et al.*, "Analysis of the nonrandom two-liquid model for prediction of liquid–liquid equilibria," *Journal of Chemical & Engineering Data*, vol. 59, no. 8, pp. 2485–2489, 2014.
- [22] O. Bacha, A. Hasseine, and M. Attarakih, "Measurement and correlation of liquid–liquid equilibria for water + ethanol + mixed solvents (dichloromethane or chloroform + diethyl ether) at $T = 293.15$ K," *Physics and Chemistry of Liquids*, vol. 54, no. 2, Mar. 2016, doi: 10.1080/00319104.2015.1079193.
- [23] H. Renon and J. M. Prausnitz, "Local compositions in thermodynamic excess functions for liquid mixtures," *AIChE journal*, vol. 14, no. 1, pp. 135–144, 1968.

- [24] S. Gebreyohannes, B. J. Neely, and K. A. M. Gasem, "Generalized nonrandom two-liquid (NRTL) interaction model parameters for predicting liquid-liquid equilibrium behavior," *Industrial & Engineering Chemistry Research*, vol. 53, no. 31, pp. 12445–12454, 2014.
- [25] A. Merzougui, N. Labeled, A. Hasseine, A. Bonilla-Petriciolet, D. Laiadi, and O. Bacha, "Parameter Identification in Liquid-Liquid Equilibrium Modeling of Food-Related Thermodynamic Systems Using Flower Pollination Algorithms," *The Open Chemical Engineering Journal*, vol. 10, no. 1, Apr. 2016, doi: 10.2174/1874123101610010059.
- [26] A. Boultif, A. Kabouche, and S. Ladjel, "Application of Genetic Algorithms (GA) and Threshold Acceptance (TA) to a Ternary Liquid-Liquid Equilibrium System," *International Review on Modelling and Simulations (IREMOS)*, vol. 9, no. 1, Feb. 2016, doi: 10.15866/iremos.v9i1.8029.
- [27] N. Bouneb and A. H. Meniai, "Temperature effect on the interaction parameters of GC-NRTL model using the genetic algorithm," *Chemical Engineering Transactions*, vol. 35, pp. 1273–1278, 2013.
- [28] W. Arlt, M. E. A. Macedo, P. Rasmussen, and J. M. Sorensen, *Liquid-liquid equilibrium data collection*. Dechema, 1979.
- [29] J. M. Prausnitz and F. W. Tavares, "Thermodynamics of fluid-phase equilibria for standard chemical engineering operations," *AIChE journal*, vol. 50, no. 4, pp. 739–761, 2004.
- [30] J. Gmehling and U. Onken, "Vapor-liquid equilibrium data collection. Aqueous-organic systems," 1977.
- [31] J. M. Sorensen, "Liquid-liquid equilibrium data collection," *DECHEMA Chem. Ser.*, vol. 2, pp. 595–605, 1980.
- [32] C. C. Chen, "Molecular thermodynamics for pharmaceutical process modeling and simulation," in *Chemical Engineering in the Pharmaceutical Industry: R&D to Manufacturing*, John Wiley and Sons, 2010, pp. 505–519.
- [33] J. Chen, L.-P. Duan, J.-G. Mi, W.-Y. Fei, and Z.-C. Li, "Liquid-liquid equilibria of multi-component systems including n-hexane, n-octane, benzene, toluene, xylene and sulfolane at 298.15 K and atmospheric pressure," *Fluid Phase Equilibria*, vol. 173, no. 1, pp. 109–119, 2000.
- [34] J. Chen, J. Mi, W. Fei, and Z. Li, "Liquid-liquid equilibria of quaternary and quinary systems including sulfolane at 298.15 K," *Journal of Chemical & Engineering Data*, vol. 46, no. 1, pp. 169–171, 2001.
- [35] J. Kennedy and R. Eberhart, "Particle swarm optimization," 1995. doi: 10.1109/ICNN.1995.488968.
- [36] A. Hebboul and F. Hachouf, "Improving Kernel soft Subspace Clustering Algorithms using a Particle Swarm Optimization," 2016. doi: 10.1145/3038884.3038887.
- [37] N. K. Jain, U. Nangia, and J. Jain, "A review of particle swarm optimization," *Journal of The Institution of Engineers (India): Series B*, vol. 99, no. 4, pp. 407–411, 2018.
- [38] M. Schmitt and R. Wanka, "Particle swarm optimization almost surely finds local optima," *Theoretical Computer Science*, vol. 561, pp. 57–72, 2015.
- [39] Y. H. Robinson and M. Rajaram, "Energy-aware multipath routing scheme based on particle swarm optimization in mobile ad hoc networks," *The Scientific World Journal*, vol. 2015, 2015.
- [40] B. Yao, B. Yu, P. Hu, J. Gao, and M. Zhang, "An improved particle swarm optimization for carton heterogeneous vehicle routing problem with a collection depot," *Annals of Operations Research*, vol. 242, no. 2, pp. 303–320, 2016.
- [41] M.-H. Golbon-Haghighi, H. Saeidi-Manesh, G. Zhang, and Y. Zhang, "Pattern Synthesis For The Cylindrical Polarimetric Phased Array Radar (CPPAR)," *Progress In Electromagnetics Research M*, vol. 66, 2018, doi: 10.2528/PIERM18011016.
- [42] Y. Wu and Q. Song, "Improved Particle Swarm Optimization Algorithm in Power System Network Reconfiguration," *Mathematical Problems in Engineering*, vol. 2021, Mar. 2021, doi: 10.1155/2021/5574501.
- [43] X. Liang, W. Li, Y. Zhang, and M. Zhou, "An adaptive particle swarm optimization method based on clustering," *Soft Computing*, vol. 19, no. 2, pp. 431–448, 2015.

- [44] F. Marini and B. Walczak, "Particle swarm optimization (PSO). A tutorial," *Chemometrics and Intelligent Laboratory Systems*, vol. 149, pp. 153–165, 2015.
- [45] R. Poli, J. Kennedy, and T. Blackwell, "Particle swarm optimization," *Swarm Intelligence*, vol. 1, no. 1, Oct. 2007, doi: 10.1007/s11721-007-0002-0.
- [46] Eberhart and Yuhui Shi, "Particle swarm optimization: developments, applications and resources," 2001. doi: 10.1109/CEC.2001.934374.
- [47] Z. Li, K. H. Smith, K. A. Mumford, Y. Wang, and G. W. Stevens, "Regression of NRTL parameters from ternary liquid–liquid equilibria using particle swarm optimization and discussions," *Fluid Phase Equilibria*, vol. 398, pp. 36–45, 2015.
- [48] İ. Yalın, S. Çehreli, A. E. Andreatta, and A. Senol, "Phase Equilibria of Ternary Liquid–Liquid Systems (Water + C1–C4 Monocarboxylic Acids + Dibutyl Ether) at Three Different Temperatures: Modeling with A-UNIFAC," *Journal of Solution Chemistry*, vol. 49, no. 7–8, Aug. 2020, doi: 10.1007/s10953-020-01006-x.
- [49] A. H. Meniai and A. Gouaoura, "Modeling Of Liquid-Liquid Equilibrium Data and Estimation of New Binary Interaction Parameters for NRTL Model for the Quaternary System Water/Ethanol/1-Butanol/KCL at 298.15 K," *Politeknik Dergisi*, vol. 20, no. 1, pp. 129–135, 2017.
- [50] Y. Moudjari, W. Louaer, and A.-H. Meniai, "Modeling of solid-liquid equilibria using a group based NRTL equation," *Chemical Engineering Transactions*, vol. 43, pp. 1867–1872, 2015.
- [51] A. Hasseine, A. Kabouche, A.-H. Meniai, and M. Korichi, "Salting effect of NaCl and KCl on the liquid–liquid equilibria of water+ ethyl acetate+ ethanol system and interaction parameters estimation using the genetic algorithm," *Desalination and Water Treatment*, vol. 29, no. 1–3, pp. 47–55, 2011.
- [52] M. Abdelkrim and R. Slimane, "A Hybrid Optimization Approach to Interaction Parameter Identification in thermodynamic model problems," *Journal of New Technology and Materials*, vol. 9, no. 1, pp. 16–21, 2019.