Experimental Data and Modeling of Salt Effect on Liquid-Liquid Equilibrium of the Ternary (Water+1-Propanol+Hexane) System at 298K

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ABSTRACT: *The effect of NaCl on the LLE data for the ternary system, water + 1-propanol + hexane, were determined at 298Kunder atmospheric pressure. The curve of solubility and tie-line data of this system were determined by experimental analysis. The experimental results showed that the addition of NaCl significantly affected the two-phase region of the ternary system, the enlargement of the two-phase region occurred with an increase of salt concentration in the initial aqueous phase. Distribution coefficients and separation factors were also calculated and compared at different NaCl concentrations. In addition, the experimental tie-line data were correlated with the NRTL model. Also, the parameters of this model were estimated with five nature-inspired metaheuristic solvers. These algorithms are Genetic Algorithms (GA), Monkey- Krill Herd Hybrid (MAKHA), Intelligent Firefly Algorithm (IFA), Cuckoo Search (CS), and Harmony Search Algorithm(HAS). The capabilities and limitations of these solvers have been analyzed. Results showed that all algorithms outperformed, in particular, MAKHA give the best efficiency-reliability for the prediction of LLE.*

KEYWORDS: *Salt effect; LLE; Nature-inspired algorithm; NRTL.*

INTRODUCTION

Propanol (*Propyl Alcohol*) used as a solvent and cleaning agents in the pharmaceutical industry mainly for resins and cellulose esters, as well as in the production of feed additives, synthetic spices and pharmaceutical industry. In other hand, it is used as a chemical intermediate, employed for medicine and pesticide. In addition, 1-propanol has high octane numbers and it is suitable for engine fuel usage [1].

Due to hugely expensive production of propyl alcohol, the recovery of this alcohol from aqueous solution is very important. Solvent extraction processes have been widely used on the production scale for liquid–liquid separations. In this process, a solution is brought into contact with a second liquid that is immiscible or partially miscible with the first one. One or more components can transfer from the solution into the solvent [2,3].

The addition of dissolved salts in the aqueous mixture causes us to alter the equilibrium composition of this mixture. This phenomenon is often referred to as the salting-out effect, which induces quantitative changes

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of the solute distribution coefficient from aqueous phase in the presence of a salt [4-6].

Salting-out can be used to improve separation in processes in chemical engineering such as,in solvent extraction to alter the miscibility gaps, in distillation to shift favorably azeotropic conditions if they may occur, in absorption and fractional crystallization to alter the distribution coefficients[4-9].In order to design and optimize the separation column for recovery of propanol from aqueous solution, a wide variety of information is required. One of the most fundamentally important information is the Liquid-Liquid Equilibrium (LLE) data. Various activity coefficient models, such as Non-Random Two Liquid (NRTL) and universal quasi chemical (UNIQUAC) can be used to predict the LLE data. These models require proper binary interaction parameters (τ_{ij}). These parameters are usually identified from fitting by correlating reliable LLE data via optimization of a suitable objective function [10-20].

The mathematical modeling of for solving thermodynamic phase equilibrium has grown considerably in recent years. Merzougui et al.[10-15] utilized the genetic algorithm, harmony search algorithm, flower pollination algorithm , hybrid genetic algorithm and Backtracking Search optimization to estimate the binary interaction parameters for the NRTL and UNIQUAC models in multi-component LLE systems. They found that all optimization solvers offers a reliable performance for solving these thermodynamic calculations. *Bhargava et al.*[16], have applied Cuckoo Search (CS) algorithm for solving phase stability, phase equilibrium and reactive phase equilibrium problems. They found that CS offers a reliable performance for solving these thermodynamic calculations and is better than other metaheuristics for phase equilibrium modeling. Ferrari et al.[17], have applied SA and PSO algorithms for LLE of the NRTL and the UNIQUAC models for binary and multi-component LLE systems and showed that both algorithms were capable of modeling LLE data.

Fernández-Vargaset al.[19] applied Ant Colony Optimization (ACO) for parameter estimation, phase equilibrium and phase stability problems and showed that this algorithm is capable of modeling liquid–liquid equilibrium data. *Fateen et al.* [20] have compared the efficiency of eight optimization solvers for phase stability and phase equilibrium problems. These solvers are the intelligent firefly (IFA), bat (BA), Artificial Bee Colony (ABC), MAKHA (a hybrid between monkey algorithm and krill herd algorithm), Covariance Matrix Adaptation Evolution Strategy (CMAES), Cuckoo Search (CS), Magnetic Charged System Search (MCSS) and BBPSO. The results clearly showed that CS is the most reliable of all tested optimization methods as it successfully solved all thermodynamic problems tested in the study.

In recent years, several research studies have addressed the experimental LLE data and the interaction parameter identification problem of ternary system {water + propanol + solvent} with or without salt [11, 21-36].

In this work, LLE data for the (water+1-propanol+hexane) ternary system in the presence of sodium chloride at three different mass percentages of 5, 10 and 15% are to be obtained and used to obtain the binary parameters of the NRTL activity coefficient model using five nature inspired metaheuristics solvers. These solvers are: Genetic algorithms (GA), Monkey- Krill Herd Hybrid (MAKHA), Intelligent Firefly Algorithm (IFA), Cuckoo Search (CS) and Harmony Search Algorithm (HAS). The capabilities and limitations of these solvers have been systematically analyzed and compared. Our results showed that all optimization solvers of fers an outstanding performance for parameter identification problem.

EXPERIMENTAL SECTION

Chemicals

All the reagents, 1-propanol, hexane and sodium chloride, were supplied by Fluka Chemicals (Germany). The purities of these liquid compounds were greater than 99 %. The salt (NaCl) compounds were dried in an oven until the weight remained as a constant before being used. The measured refractive indices (n_D) of pure components at T = 298K along with the literature data available [37], were shown in Table 1.

Apparatus and procedure

The procedure for the determination of the binodal curve and the tie lines at 298 K of the system water (1) + 1-propanol (2) + hexane (3) was similar to that previously papers [38-41]. The experimental procedure for the determination of the solubility data of a salt (NaCl) containing ternary liquid system is similar to the procedure adopted for the salt free solution, except that water was replaced by aqueous salt solution. Quantities of salt

Table 1: Refractive index (n_D) at T = 298K.

Component	Refractive index (n_D)	
	Exp	Lit
Water	1.3333	1.3328
1-Propanol	1.3872	1.3837
Hexane	1.3738	1.3723

Standard uncertainties uare: u=(n_D) = ±1.10^{-4}

wereadded to make corresponding mixtures of different salt mass percentages (5, 10 and 15% of the total water weight in the mixture).

In other hand, for the determination of the tie lines data, feed samples were prepared by mixing appropriate amounts of water, 1-propanol, hexane and salt in an equilibrium cell at constant temperature by using a thermostatic bath (Wise Circu with an accuracy of ± 0.1K)., and the components were weighed on an analytical balance ((Model Nahita YP402N, accurate to±0.001 g).

These mixtures were vigorously agitated with a magnetic stirrer for 3 h, to allow an intimate contact between the phases, and the equilibrium was achieved by letting the mixture rest for 24 h. After quantitative gravity separation, both phases were then separated and each phase was weighed. The analysis procedure consisted of analyzing samples from both phases by measuring the respective refractive indexes using DR-A1 Digital AbbeRefractometer at equilibrium with an accuracy of ±0.0004n_D. The measuring of refractive indexes was repeated three times, and the average was used.

Prior to these refractometer measurements, calibration plots of refractive index giving the change of the refractive index with concentration of the solution at 298K have been used to read the concentrations of each constituent in organic phase. The concentrations in the aqueous phase solution were obtained from material balance. The amounts of the salt in the aqueous and organic phases were determined by evaporation and material balance, respectively [5, 42]. However this may be imprecise in some cases but remains acceptable as long as the amount of dissolved salt in the organic phase is very low.

THERMODYNAMIC MODELING OF THE LLE DATA

The relationship of the LLE can be represented with an activity coefficient model. Each composition of the two phases can be thermodynamically modeled by phase equilibria of components in two coexistent liquid phases as follows:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \tag{1}$$

$$\sum_{i=1}^{Nc} x_i^I - 1 = 0 \tag{2}$$

$$\sum_{i=1}^{Nc} x_i^{II} - 1 = 0 \tag{3}$$

Where $x_i^I, x_i^{II}, \gamma_i^I$ and γ_i^{II} are the mole fraction and activity coefficient of component*i* in phases *I* and *II*, respectively.

The thermodynamic model used in this work is the NRTL (Non-Random Two Liquid model) described in the literature [43]. The NRTL activity coefficient model for component *i* are expressed as follows:

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ji}}{\sum_{k=1}^{n} G_{ki} x_k} \left(\tau_{ji} - \frac{\sum_{j=1}^{n} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{n} G_{ki} x_k} \right) \tag{4}$$

The adjustable parameters of NRTL model can be estimation using thefollowing expressions [44]:

$$\tau_{ij} = \frac{\Delta g(ij)}{R \cdot T} = \frac{A_{ij}}{T} \tag{5}$$

$$G_{ij} = \exp\left(\alpha_{ij} \tau_{ij}\right) \tag{6}$$

$$\alpha_{ij} = \alpha_{ji} \tag{7}$$

Where, α_{ij} is the non randomness parameters were assumed to be 0.2 and $A_{ij}$are the adjustable binary interaction parameters of NRTL equation. These parameters can be estimated with experimental data, by using the procedure in section 5.

Nature-inspired metaheuristic algorithms for parameter estimation of NRTL model

Five nature-inspired metaheuristics were applied f or solving challenging engineering optimization problems including parameter identification problem in liquid-liquid equilibrium (LLE) modeling of ternary system (water+1-propanol+hexane) with and with-out salt.

As stated, these optimization methods are: Genetic Algorithms (GA), Monkey- Krill Herd Hybrid (MAKHA), Intelligent Firefly Algorithm (IFA), Cuckoo Search (CS) and Harmony Search Algorithm (HAS).

Brief introductions of selected algorithms are reported in this paper. Interested readers are referred to the primary sources of those methods for more details [45-49]. Specifically, GA [34] is abio-inspired algorithm that imitates the behavior of surviving individual to optimize solutions through mutation, crossover, and selection operations. MAKHA [45] is a hybrid between Monkey Algorithm, which is based on the behavior of a monkey searching for better food sources by climbing up trees, and Krill-Herd Algorithm which simulates the herding behavior of krill individuals. IFA [46, 47] is a variant of Firefly Algorithm and it is an algorithm inspired by the flashing behavior of fireflies to attract other fireflies. CS [48] is an optimization algorithm inspired by the obligate brood parasitism of some cuckoo species by laying their eggs in the nests of other host birds. Finally, HAS [49] is based on natural musical performance process of searching for a perfect state of harmony such as during jazz improvisation. MATLAB® codes of all the optimization algorithms were used in this work. GA code is obtained from MATLAB® file exchange server. The others codes used for MAKHA, IFA, CS and HAS were developed by the authors or obtained from their developers.

RESULTS AND DISCUSSION

The miscibility curves

The experimental miscibility curve of ternary system (water + 1-propanol + hexane)for the different cases (0%, 5%, 10% and 15% NaCl) at 298K are presented in Table S.1 and shown in Fig. 1. The investigated ternary system exhibits type-1 behavior of liquid-liquid equilibrium [50]. Moreover, the Fig. 1 shows the effect of the addition of the sodium chloride on miscibility curve. From these diagrams it can be noticed that the region of heterogeneity increases on adding the salt on the (water + 1-propanol + hexane) ternary mixture. The addition of salt to the system is beneficial for separation and enlarges the operation range of extraction process. This can be explained by the fact that NaCl molecules compete with those of 1-propanol for water molecules, causing, therefore, a deficit in the solvation shells around the organic solute which may become free to move and migrate into the n-hexane riche phase.

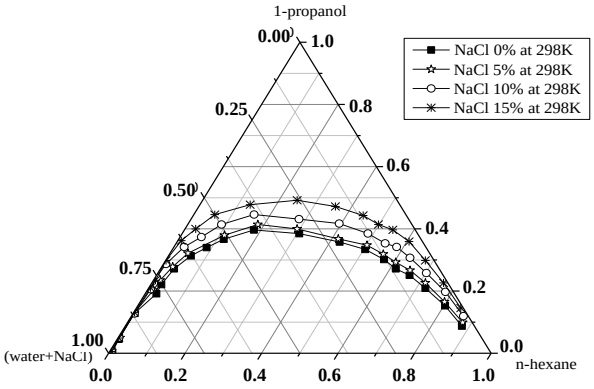

Fig. 1: Comparison of the LLE phase diagram for water (1) + 1-propanol (2) + hexane (3) + NaCl (4) at different concentration of NaCl at 298 K.

The measured tie line data of the LLE for the investigated ternary system were also determined at 298K and atmospheric pressure are listed in Table S.2.

To estimate the capability of hexane at different NaCl concentrations to separate 1-propanol, the distribution ratios, D_1 for water and D_2 for 1-propanoland the separation factor (S), for hexane were calculated. The distribution ratios (D_i) and the separation factor were determined as follows [11]:

$$D_i = \frac{w_{i3}}{w_{i1}} \tag{8}$$

$$S = \frac{D_1}{D_2} \tag{9}$$

Where, w_{i1} *and* w_{i3} are the mass fraction of the i^{th} component in the water-rich phase and the hexane-rich phase respectively;

The values of $D_2$are shown in the Table 3 and in Fig. 2. The results of the distribution coefficient shows that the value of the distribution coefficient varies from 1.7507 to 6.3535, 2.6504 to 6.7810, 3.3417 to 13.775 and 5.1255 to 16.4079 when the mass of the added sodium chloride are 0, 5, 10 and 15% of the initial water respectively. Fig. 2 presents a comparison between the results for salt-free system and with the presence of NaClat temperature at 298K. It can be concluded from the plot that the salt added has a significant trend for an increase comparing with the salt-free system. When NaCl added, each salt ion attacks surrounding water molecules, forming hydration shells. Thus, improve migrate of solute to the n-hexane riche

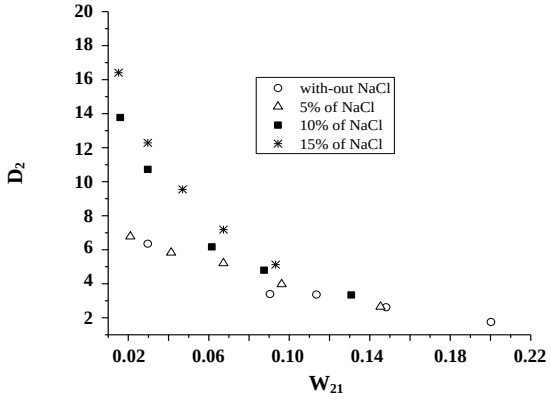

Fig. 2: Plot of the 1-propanol (D2) distribution coefficients* vs. *acetic acid mass fraction in the aqueous phase at different concentration ofNaCl at 298.15 K.

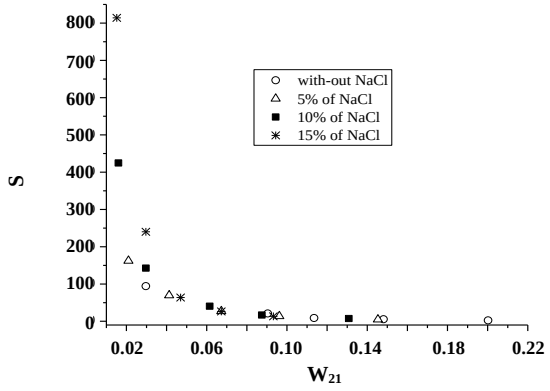

Fig. 3: Plot of separation factor* vs. *mass fraction of 1-propanol in the aqueous phase at different concentration of NaCl at 298.15 K.

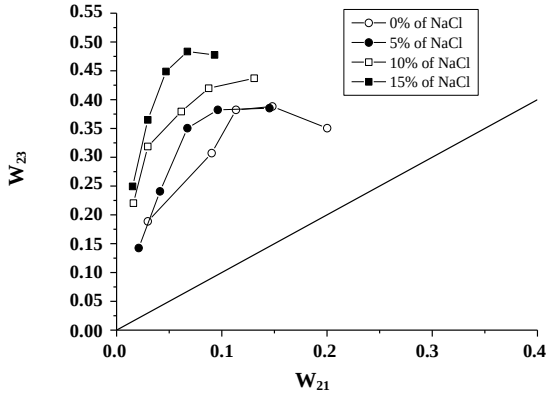

Fig. 4: Effect of NaCl on the equilibrium distributions for different salt concentration percentages for the system water.

phase[51].The selectivity curves have a similar behavior (see Fig. 3) with the highest values corresponding to the system with mass percentages15 % NaCl. The distribution coefficients and the selectivity's trends are as follows:

$$D_2^{15\%} > D_2^{10\%} > D_2^{5\%} > D_2^{0\%}$$
$$S^{15\%} > S^{10\%} > S^{5\%} > S^{0\%}$$

Fig. 4, shows the effect of the different salt percentages on the (water + 1-propanol + hexane) ternary system at 298K. This Figure confirms that the addition of sodium chloride actually disrupted the distribution of the 1-propanol between the hexane and the water. We can see that the distribution curves for each percentage of salt added are always above the first bisector what indicates that a more favorable 1-propanol distribution in the organic phase than in the aqueous one. This effect can be quantitatively verified through the mean distribution coefficient of the ١-propanol presented in the Table 3. According to the above, this effect is essentially increased the heterogeneity of the mixture; this is an important factor in the design of a liquid-liquid extraction process [5].

Generally for a given mixture, only few experimental equilibrium data are available.For this reason, there are some varieties of empirical correlations that are useful for considering the reliability of the experimental tie-line data. In this work, the consistency of the obtained experimental data can be assessed graphically by means of a method based on improved *Eisen-Joffe*equation[52].

$$\log\left(\frac{w_2^{II}}{w_3^{II}}\right) = a + bw_s + (c + dw_s)\log\left(\frac{w_2^{I}}{w_1^{I}}\right) \qquad (10)$$

where, w_1^I and w_2^I represents the mass fraction of water and 1-propanol in the water-rich phase, w_2^{II} and w_3^{II} represents the mass fraction of 1-propanol and hexane in the hexane-rich phase, and w_s represents the mass fraction of NaCl in the initial salt solution. The letters *a*, *b*, *c*, and *d* are parameters of the *Eisen-Joffe* equation, these parameters are depends on the nature of the mixture and the temperature. Furthermore, *b* and *d* are relevant to the salt concentration, while *a* and*c* are not. Parameters of the *Eisen-Joffe*equation in Eq. (10) were determined graphically using the tie-line data for investigated ternary mixture are listed in Table 4. All linear correlation coefficients (R^2) are close to one; these values indicate

Table 4: Values of the Eisen-Joffe equation parameters for the system of water(1)+ 1-propanol (2) +hexane(3) `with various salt at 298.15K and atmospheric pressure.

w_s	a	b	c	d	R^2
0	2.7378		1.2325		0.9062
0.05		6.8460		1.058	0.9798
0.10		-2.788		-3.235	0.9566
0.15		5.1430		-0.763	0.9914

ofa better goodness of fit for the LLE data of the considered systems.

Parameters identification and data correlation

All adjustable binary interaction parameters for NRTL model have been obtained from the experimentally equilibrium compositions data for water+1-propanol+hexane and sodium chloride mixture at various salt concentration, by minimizing the differences between the experimental and calculated mass fractions for each of the components over all tie lines, using the root-mean square deviation (RMSD), defined as [11,44]:

$$\mathrm{RMSD}\left(\frac{\sum_{j=1}^{M_t}\sum_{i=1}^{N_C}\left(\left(w_{ij}^{exp}-w_{ij}^{calc}\right)_I^2+\left(w_{ij}^{exp}-w_{ij}^{calc}\right)_{II}^2\right)^{1/2}}{2M_tN_C}\right) \quad (11)$$

Where, $M_t$and $N_C$are the number of tie lines and the number of components, w^{exp} and w^{cal} indicates the experimental and calculated mass fraction, subscripts *I, II,i*and *j* represent thephases at equilibrium, the constituents and the tie lines, respectively. Results of interaction parameters identification using tested metaheuristics algorithms are summarized as follows:

The performances of the five metaheuristics algorithms with and without a local optimizer were quantified and compared based on three metrics: the stopping conditions or the maximum number of iterations ($Iter_{max}$), the RMSD values and the mean modeling errors for the prediction for the NRTL model after the minimization of Eq. (11).

For illustration, the convergence profiles (logarithmic scale) of the stochastic solvers without local optimization, during the solving NRTL parameter estimation for water + 1-propanol + hexane + NaCl with (15%) mass fractions of initial water at 298 K are reported in Fig. 5.It is clear that the performance of the five heuristic optimization techniques increased with the increments of $Iter_{max}$ and may reach a high precision in the solution obtained. For instance, Fig. 5 shows that MAKHA converged to an optimal solution for speed-based evaluation compared to other four techniques. It should be noted that, the intensification step for Harmony Search Algorithm is needed more iterations steps for convergence and for improving the accuracy of final solutions

The efficiency of the five nature-inspired algorithms without local optimization has been compared, in terms of RMSD values during the parameter identification of NRTL model. For illustration, Fig. 6 shows the results of GA, CS, IFA, MAKHA and HSA for the LLE calculation of ternary system (water + 1-propanol + hexane + NaCl) at 298 K. According to Fig. 6, all stochastic algorithms showed a good reliability for the parameter estimation problem and their average RMSD ranged from 0.003 to 0.008.

On the other hand, the performance of the five algorithms in combination with two different local optimizers (i.e., Quasi-Newton method and Nelder–Mead method) for the parameter identification problem are reported in Fig. 7. From this Figure, it can be seen that the application of these local optimizers improves the precision of solution obtained for GA, CS, HSA solvers due to the capability of local optimizer for finding a high precision of the global solution in few function evaluations. For example, the three solvers (i.e., GA, CS and HSA) without the local optimization showed a low average RMSD values (<0.008 for HSA, <0.007 for GA and <0.0055 for CS) for finding the optimal solution at the maximum number of iterations($Iter_{max}$), see Fig. 7, while these three solvers with different local optimizers can reduce the average RSMD values up to 20% In particular, MAKHA and IFA are offers the best performance to find the NRTL model parameters for electrolyte system even without using the local intensification strategy.

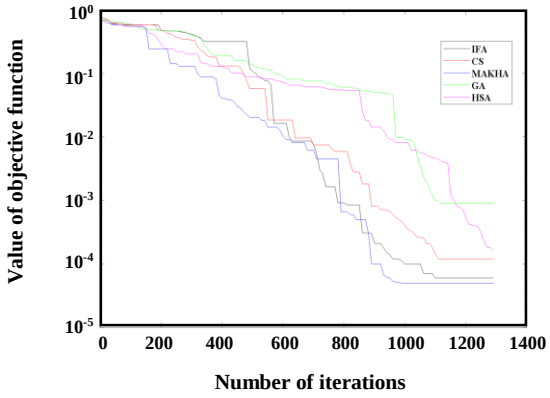

Fig. 5: Convergence profiles of nature-inspired metaheuristics for the parameter estimation of activity coefficients of water +1-propanol + hexane +NaCl(15%) at 298K using NRTL model.

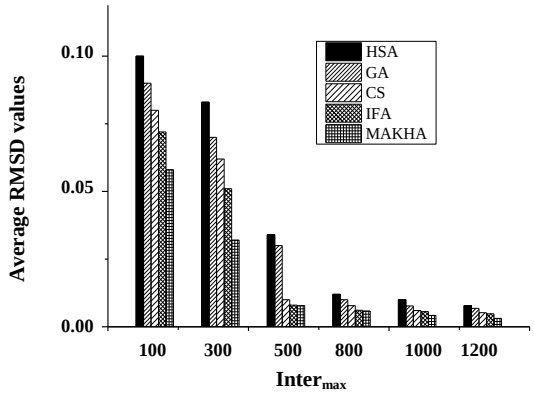

Fig. 6: Performance of several stochastic optimization solvers for the parameter estimation of activity coefficients of water +1-propanol + hexane +NaCl at 298K using NRTL model.

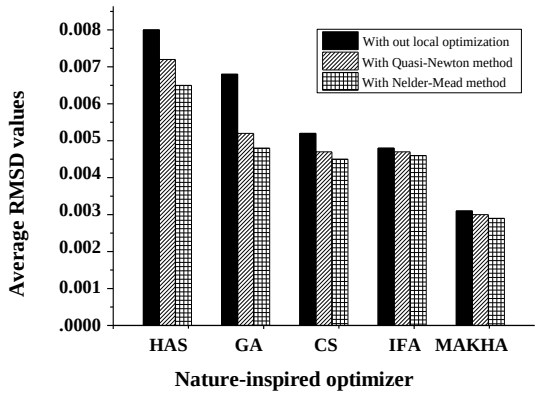

Fig. 7: Average RMSD values of nature-inspired metaheuristics with and without local optimizationfor the parameter estimation of mean activity coefficients of water +1-propanol + hexane +NaCl at 298K using NRTL model.

Finally, the efficiency of selected nature-inspired methods has been compared, in terms of the modeling errors during the parameter identification of NRTL model. Data modeling errors are illustrated in Fig. 8 by plotting the experimental mass fraction of LLE in both phases versus the corresponding calculated data for all tie lines used in the binary parameter identification with NRTL model. Results show that the determination coefficients (R^2)>0.99 for all optimization solvers. In additionally, the modeling errors ranged from 15.85 to 46.12% for HSA, 14.27 to 41.54 % for GA, 12.59 to 33.38% for CS, 10.52 to 29.11% for IFA and 9.72 to 25.77% for MAKHA, respectively.

The mean modeling errors for the prediction of phase diagrams for each salt concentration are also graphically represented in Fig. 9. As depicted in the Fig. 9, the mean modeling errors between experimental measurements and predicted LLE tie lines increased with increasing of salt concentration for all optimization solvers. This increase in mean modeling error can be attributed to the inability of the NRTL model to specific the interactions between the molecules and ions (solvation).

In summary, we can conclude that the nature-inspired algorithms are a robust optimization technique for the identification of NRTL model parameters for predicting and representing the LLE of (water + 1-propanol + hexane + NaCl) mixture. In particular, MAKHA solver showed high performance (speed convergence, lowest values of RMSD and low modeling errors) for LLE modeling. The phase diagrams of ternary system using the best interaction parameters of NRTL model (Table5) are reported in Figs. 10-13. The comparison of tie-line compositions indicated that the experimental and calculated LLE data agreed very well using this activity coefficient model.

CONCLUSIONS

LLE data for the ternary system of (water + 1-propanol + hexane), with and without salt of NaCl, were measured at 298K and under ambient pressure.According to the results, the effect of the NaCl addition at different concentrations on the original ternary system was observed by the increase of the two-phase region and the changes in the slopes of the experimental tie lines. In additionally, the addition of NaCl showed to be effective in modifying the distribution of a solute between two partially miscible solvents in favor

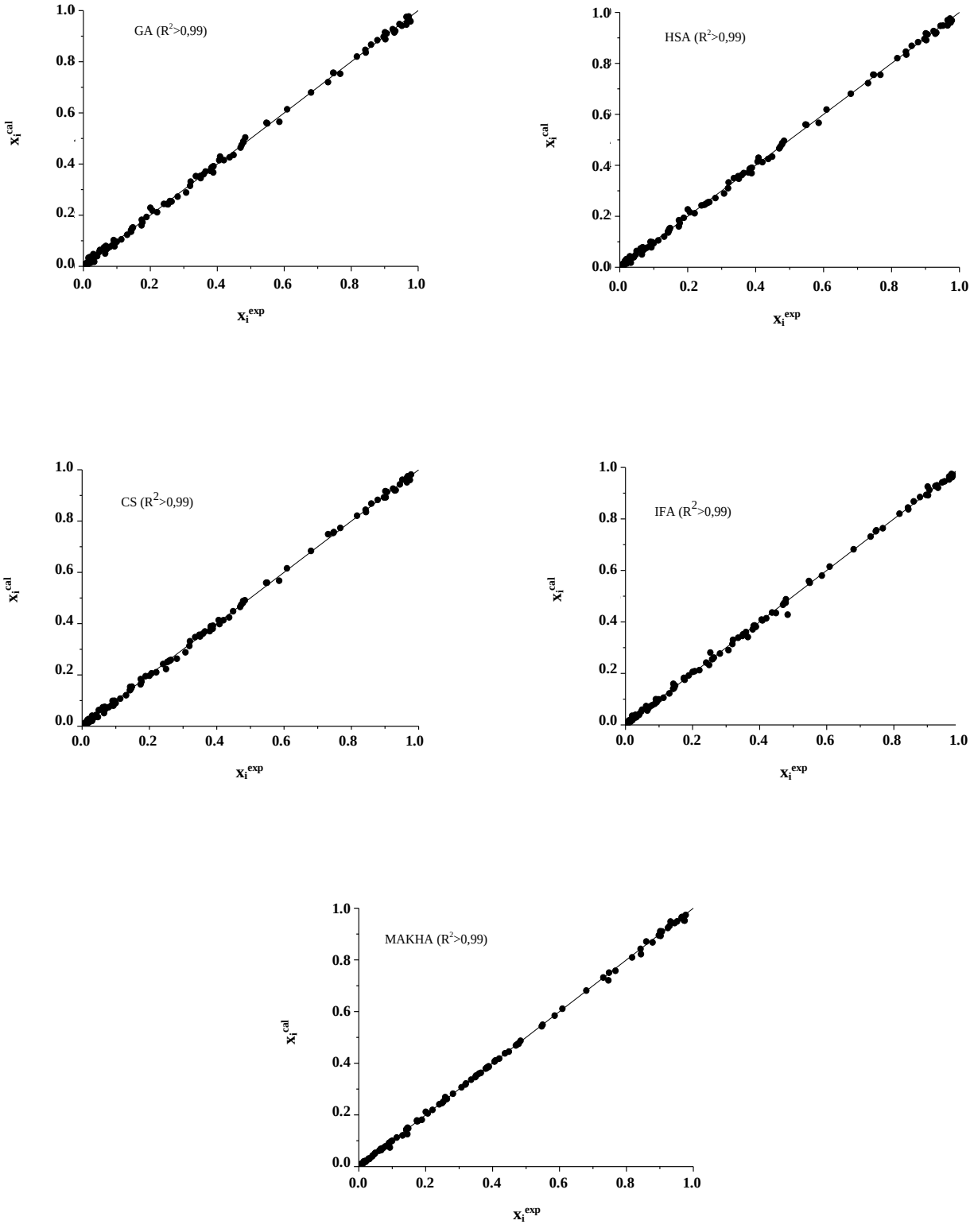

Fig. 8: Experimental and predicted LLE data of water+1-propanol+hexane+NaCl ternary systems modeled with NRTL.

Table 5: NRTL (α=0.2) binary interaction parameters (A_{ij} and A_{ji}) and RMSD values for the systems investigated.

Ternary system	i-j	A_{ij}/K	A_{ji}/K	RMSD (%)
Water +1-Propanol+ Hexane	1-2	1021.2508	-581.3570	0.125
	1-3	-953.8104	54.0581	
	2-3	793.5790	1060.2205	
Water +1-Propanol+ Hexane+5%NaCl	1-2	1153.4520	-782.6604	0.248
	1-3	-672.3351	68.8476	
	2-3	856.2384	1105.5560	
Water + 1-Propanol+ Hexane+10%NaCl	1-2	1186.1088	-683.4578	0.265
	1-3	-720.6848	72.0581	
	2-3	753.9854.	1234.5920	
Water + 1-Propanol+ Hexane+15%NaCl	1-2	1183.7852	-568.8545	0.285
	1-3	-684.0214	122.2508	
	2-3	682.5488	1008.4258	

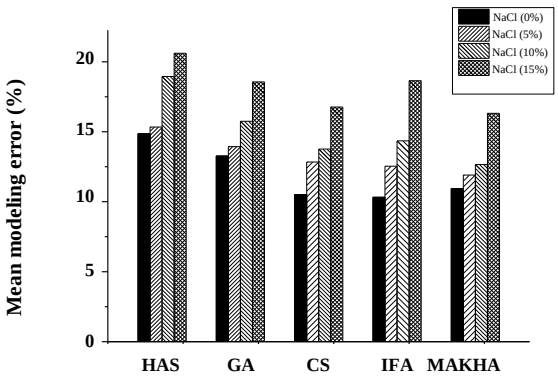

Fig. 9: Mean modeling errors (%) of NRTLfor (water+ 1-propanol+hexane+NaCl) ternary system.

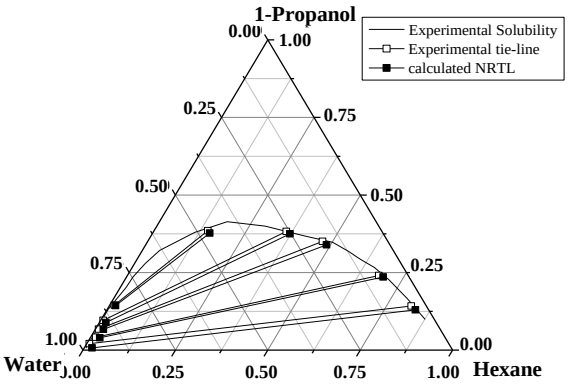

Fig. 11: LLE phase diagram for water (1) + 1-propanol (2) + hexane(3)+5%NaCl at 298K.

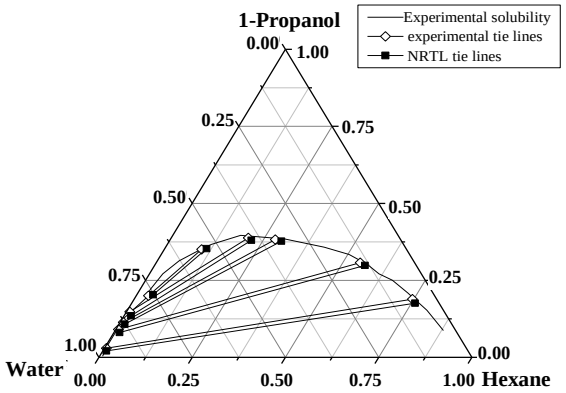

Fig. 10: LLE phase diagram for water (1) + 1-propanol (2) + hexane (3) at 298K.

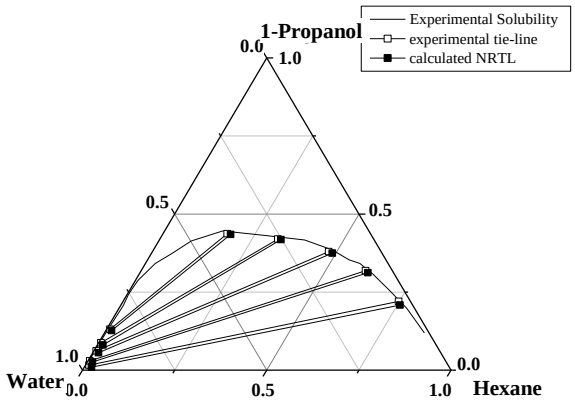

Fig. 12: LLE phase diagram for water (1) + 1-propanol (2) + hexane (3)+10%NaCl at 298K.

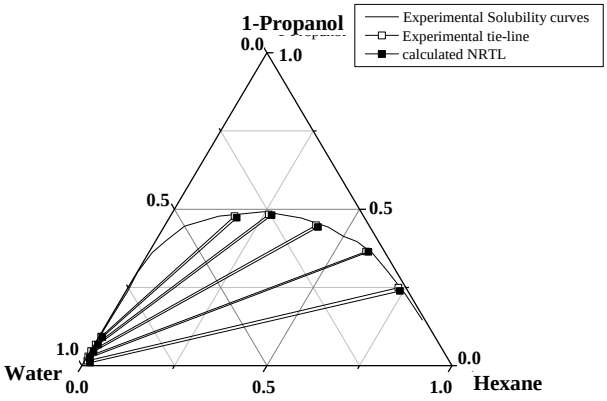

Fig. 13: LLE phase diagram for water (1) + 1-propanol (2) + hexane (3)+15%NaCl at 298K.

of the extraction process of 1-propanol from aqueous solution with hexane, particularly at high NaCl concentrations (15%). The consistency of experimental tie-lines data was confirmed by the improved *Eisen-Joffe* equation; showing a high level of agreement.

Finally, an integrated optimization–simulation algorithmbased on five stochastic optimization techniques were employed to correlate the experimental results based on NRTL model and to find the model parameters. The efficiency of these stochastic methods was analyzed and compared; the results showed that all algorithms offered the best performance for solving the model parameters. However, Monkey- Krill Herd Hybrid (MAKHA) Optimization technique outperformed other stochastic methods used for NRTL parameter identification and can be considered as the best solver for solving LLE calculation problem. The agreement between calculated and experimental data results was excellent based on RMSD criterion.

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