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Determination of Ternary Systems Bisphenol A-Water-Organic Solvent Interaction Parameters by Genetic Algorithm Approach

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Abstract: An equilibrium phase study is very important for the design, optimization, and control of transformation and separation operations. The investigation of liquid-liquid or liquid-vapor equilibrium has been the subject of much interest in the chemical and petrochemical industry in recent years. Optimizing separation processes is one of the most important areas of process design and numerous types of research both practical and theoretical. The objective of the present work is twofold. First, it involves relying on experimental work to determine data of the liquid-liquid equilibrium (conodals) of ternary systems: {Bisphenol A (1) + Water (2) + Butan-1-ol (3)}, {Bisphenol A (1) + Water (2) + Cyclohexanol (3)} and {Bisphenol A (1) + Water (2) + Cyclohexane (3)}. In the second objective, the experimental results described in the first part were used to calculate interaction parameters of thermodynamic models such as NRTL and UNIQUAC in each phase base on a genetic algorithm technique programmed on MATLAB software. The results of correlations obtained from the experimental equilibrium data for the ternary systems were compared with those obtained from experimental data. The analysis of the results shows a very good agreement between the experimental data and the results obtained after optimization that demonstrates the reliability of the estimated interaction parameters as well as the capacity of NRTL and UNIQUAC models. Therefore, one can retain that the optimization method by genetic algorithms is a reliable method for the design and the simulation of processes.

Keywords: Liquid-Liquid Equilibrium, Genetic Algorithms (GA), Interaction Parameters

1. Introduction

The studies of liquid-liquid equilibrium for ternary systems are very important for both theoretical studies and industrial applications. Indeed, the knowledge of precise liquid-liquid equilibrium data for aqueous mixtures was used for the evaluation of the solvent extraction process in industrial units [1, 2]. This present study is part of the thematic of developing a viable economic method for water pollution treatment by emerging pollutants such as Bisphenol A. Indeed, Bisphenol A is an endocrine disruptor in the plastics industry and it can cause endocrine disruption effects in humans and animals. Therefore, the capacity of three solvents to extract Bisphenol A (BPA) through the liquid-liquid extraction process at the scale of the laboratory test bench will be tested. For that, the experimental data of liquid-liquid equilibrium such as the solubility curve, and the conodals lines will first be determine. These equilibrium data (conodals) will then be correlated later using the NRTL and UNIQUAC thermodynamic models. The binary interaction parameters of these models have been obtained by the use of genetic algorithms techniques programmed on MATLAB. The solvents used in this present work are Butan-1-ol, Cyclohexane, and Cyclohexanol.

2. Theoretical Studies

2.1. Optimization Method

The experimental measurement of phase equilibrium is not easy. Therefore, modeling such equilibrium is inevitable and even essential for the calculation of systems whose processes involve particularly separate techniques that generally include different phases. This Modeling also allows a good understanding and a good analysis of systems based on the representation of equilibrium data. This allows a reduction in the number of experimental data necessary for the design of industrial processes. However, to reach a satisfactory model, it is necessary to call upon to fairly rigorous and robust tools. Most of the time, one must take into account the non-identity of the mixtures. The resolution of an optimization problem consists in exploring a research space to maximize (or minimize) a given objective function. The complexities (in size or structure) relating to the search space and the function to be maximized (or minimized) lead to the use of radically different resolution methods. As a first approximation, one can say that deterministic methods are suitable for small and complex research spaces and that a large research space rather requires stochastic research methods like genetic algorithms [3].

2.2. Genetic Algorithm

The genetic algorithms Initiated in the 1970s by JOHN Holland [4]; are optimization algorithms based on techniques derived from genetics and the mechanisms of nature such as evolution: selection, crossing, and mutation. Genetic algorithms provide solutions to problems that have no analytically or algorithmically computable solutions. According to this method, several more or less good solutions (genotypes) are created at random. These solutions are submitted to an evolutionary process according to their relevance by mimicking the natural evolution of species: the most adapted solutions, that is to say, solutions to the problem that, are optimal survive more than those that are less. Thus, the population evolves by successive generations by crossing the best solutions between each other and mutating them. Then, the genetic algorithm relaunches this process several times to tend toward the optimal solution [4]. Genetic algorithms are concerned with each individual by their genetic code. This genetic code is made up of a set of data such as chromosomes, themselves made up of genes whose perfect association characterizes the individual. Genetic operators operate at the genotypic level while the selection mechanism operates at the phenotypic level. It should be noted that the phenotype is the set of characteristic traits of an individual, while the genotype is the coding of these traits into genes [5]. To calculate the interaction parameters of NRTL and UNIQUAC models for the liquid-liquid equilibrium of this study, a calculation program based on the technique of genetic algorithms (GA) was developed on MATLAB software.

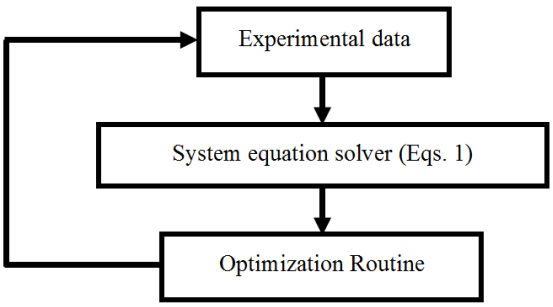

Figure 1. *Genetic algorithm procedure [5].*

2.3. NRTL (Non-Random Tow Liquids) Model

The NRTL model proposed by J. M. Prausnitz Renon [6] is based on the concept of local composition. In addition, this model has the advantage over the Wilson model of being able to represent liquid-liquid equilibrium. However, the NRTL model requires three parameters per binary system. The fundamental idea on which the NRTL model is based is the assimilation of a binary to a set of cells centered on one or the other of the two constituents [7]. This idea considers that the neighboring closest to the attraction center are distributed center randomly as a function of molecular interactions. Local molar fractions are introduced. The NRTL model can be generalized to a mixture of orders higher than two orders. Based on the experimental data, the NRTL model makes it possible to predict the liquid-liquid equilibrium data. For the calculation of this liquid-liquid equilibrium data the following equations must be solved [19]:

$$\begin{cases} x_i^E \beta + x_i^R (1-\beta) - z_{i,Feed} = 0 \\ x_i^E \gamma_i^E - x_i^R \gamma_i^R = 0 \\ 1 - \sum_{i=1}^{N_C} x_i^E = 0 \;\; i = 1, N_C \\ 1 - \sum_{i=1}^{N_C} x_i^R = 0 \end{cases} \quad (1)$$

The values to be determined are: x_i^E and x_i^R.

These same experimental data are then used to determine binary interaction parameters A_{ij} and A_{ji} by solving the following equation:

$$ln\gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{l=1}^{n} \tau_{lj} G_{lj} x_l}{\sum_{k=1}^{n} G_{kj} x_k} \right) \quad (2)$$

Where $\tau_{ij} = \frac{g_{ji} - g_{ij}}{R.T} = \frac{A_{ji}}{T}$; $G_{ij} = exp(-\alpha_{ji}.\ \tau_{ji})$; $\alpha_{ij} = \alpha_{ji}$

For the calculations, the values of the following parameters are fixed: $\alpha_{ij} = \alpha_{ji} = 0.2$.

The determination of the liquid-liquid equilibrium data for the systems studied by the NRTL models requires knowledge of the interaction parameters, which must be calculated. This calculation is done using experimental and calculated data in a function called objective function (*f*). Then minimizing this objective function, which is expressed as follows, by the genetic algorithm NSGA II:

$$min\ f = -\sum_{j=1}^{Np} \sum_{k=1}^{Nb} \sum_{i=1}^{Nc} W_{ijk} \left(x_{ki}^{cal} - x_{ki}^{Exp} \right)^2 \quad (3)$$

With W_{ijk} the weight factor of component *i* in phase *j* for

the kth equilibrium line, x^{cal} and x^{Exp} are respectively the calculated and experimental compositions [8].

2.4. UNIQUAC (Universal QUAsiChemical) Model

Abrams and Prausnitz [9] described from statistical mechanics a new UNIQUAC model on the theoretical basis of statistical thermodynamics. It should be noted that this theoretical basis is provided by the quasi-chemical network model of Guggenheim, and extended to mixtures of molecules that differ significantly in their size and shape. As in Wilson and NRTL models, local concentrations are used. Abrams and Prausnitz found that the UNIQUAC model is more precise for the liquid-vapor system. Abrams's and Prausnitz's model gives, two adjustable parameters per binary, a good representation of liquid-vapor and liquid-liquid equilibrium. These binaries consist of a wide variety of binary liquids of several mixtures, and non-electrolytes such as hydrocarbons, ketones, esters, amines, alcohols, nitriles, etc. For the UNIQUAC model, the expression of excess free enthalpy involves two terms:

1. A combinatorial term that takes into account differences in that between molecules. This combinatorial term involves two parameters of pure components: the volume (r_i) and the area (q_i) of Van Der Waals.
2. A residual term, which takes into account the interactions between molecules. This residual term has the form of a local composition term. It involves two interaction parameters per binary system (τ_{ij} and τ_{ji}). The UNIQUAC model allows predicting the liquid-liquid equilibrium data from experimental data. Solving the following, equations provides this liquid-liquid balance data [19]:

$$\begin{cases} x_i^E \beta + x_i^R (1-\beta) - z_{i,Feed} = 0 \\ x_i^E \gamma_i^E - x_i^R \gamma_i^R = 0 \\ 1 - \sum_{i=1}^{N_C} x_i^E = 0 \\ 1 - \sum_{i=1}^{N_C} x_i^R = 0 \\ i = 1, N_C \end{cases} \quad (4)$$

The values to be determined are: x_i^E and x_i^R.

Experimental data are used to determine binary interaction parameters A_{ij} et A_{ji}. These binary interaction parameters are obtained by solving the following equation:

$$ln\gamma_i = ln\frac{\phi_i}{x_i} + \frac{z}{2} q_i ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_{j=1}^{n} x_j l_j + q_i \times \left[1 - ln\left(\sum_{j=1}^{n} \theta_j \tau_{ji}\right) - \sum_{j=1}^{n} \frac{\theta_j \tau_{ji}}{\sum_{k=1}^{n} \theta_k \tau_{ki}}\right] \quad (5)$$

Where $\theta_i = (q_i x_i / q_T)$; $q_T = \sum_{k=1}^{n} q_k x_k$; $\phi_i = r_i x_i / r_T$;

$$r_T = \sum_{k=1}^{n} r_k x_k;$$

$$l_i = \frac{z}{2}(r_k - q_k) + 1 - r_k;\ \tau_{ij} = exp\left(-\frac{A_{ij}}{T}\right);\ z = 10$$

z: Coordination number of UNIQUAC model network.

The parameters r_i and q_i are linked to the molecule structure.

3. Materials and Methods

3.1. Chemicals Used

The BPA with a purity of 97%, used in this work was purchased from Alfa Aesar. The solvents used are:

1) Butan-1-ol, with 99.5% of purity has been purchased from Carlo Erba,
2) Cyclohexanol with a purity of 99%, was purchased from Merck,
3) Cyclohexane with a purity of 99.5%, was purchased from Merck,
4) Distilled water used in this work was prepared in the laboratory by the use of a water distiller.

3.2. Experimental Method

The objective of this part is to investigate the liquid-liquid equilibrium of three ternary systems (BPA –Water – Butan-1-ol), (BPA – Water –Cyclohexanol), and (BPA – Water –Cyclohexane) to a constant temperature of 30 ± 2°C and at atmospheric pressure. The isothermal solubility (binodal curve) was determined by the "cloud point method" [11, 12].

3.2.1. Construction of the Solubility Curve (Binodal)

The data determination for the construction of the solubility curve will be made with a synthetic solution of BPA with a concentration of C = 5 mg/L. The construction of binodal curves is done in two steps.

First step: Water-rich Portion of the Curve

A weighing series of binary mixtures (BPA + Water) are prepared by using an electric balance, stirring mixtures are provided by a mechanical stirrer with constant speed. The solvent is gradually added to this mixture by using a micro cruet while stirring until the occurrence of turbidity (the point where the binary mixture begins to lose its homogeneity and just after this point it is noticed the presence of two phases). The mixture obtained is weighed again. Several measures are made. The conversion of compositions for each component of the mixtures obtained in a mass fraction is calculated by using the following equation:

$$X_i = \frac{m_i}{m_T} \quad (6)$$

With, Xi mass fraction of component (*i*) (BPA, Solvent, Water) m_i initial mass (g) of component (*i*). m_T: total mass (g) of the mixture after titration.

Second Step: Solvent-rich Portion of the Curve

The same steps as the previous study are repeated. However, the difference between the two steps is: that for the 2nd step, the initial binary mixtures are (BPA + Solvent), and the third element (Water) is added by titration until the apparition of turbidity.

3.2.2. Ternary Systems Balance Lines (Conodals) Construction

The procedure involves, first, the preparation of a series of ternary blends (BPA + water + solvent) composed of 30 g of

equal mass with different concentrations [13]. At ambient temperature, each mixture is stirred vigorously with a magnetic stirrer for 4 hours to allow intimate contact between the phases. The balance is achieved by ensuring the rest mixtures are in a separating funnel of 250 mL for 8 hours. The two phases (organic and aqueous) are then separated by decantation and then weighed. After complete phase separation, an appropriate amount of each phase (aqueous and organic) is taken for analysis by high-performance liquid chromatography (HPLC).

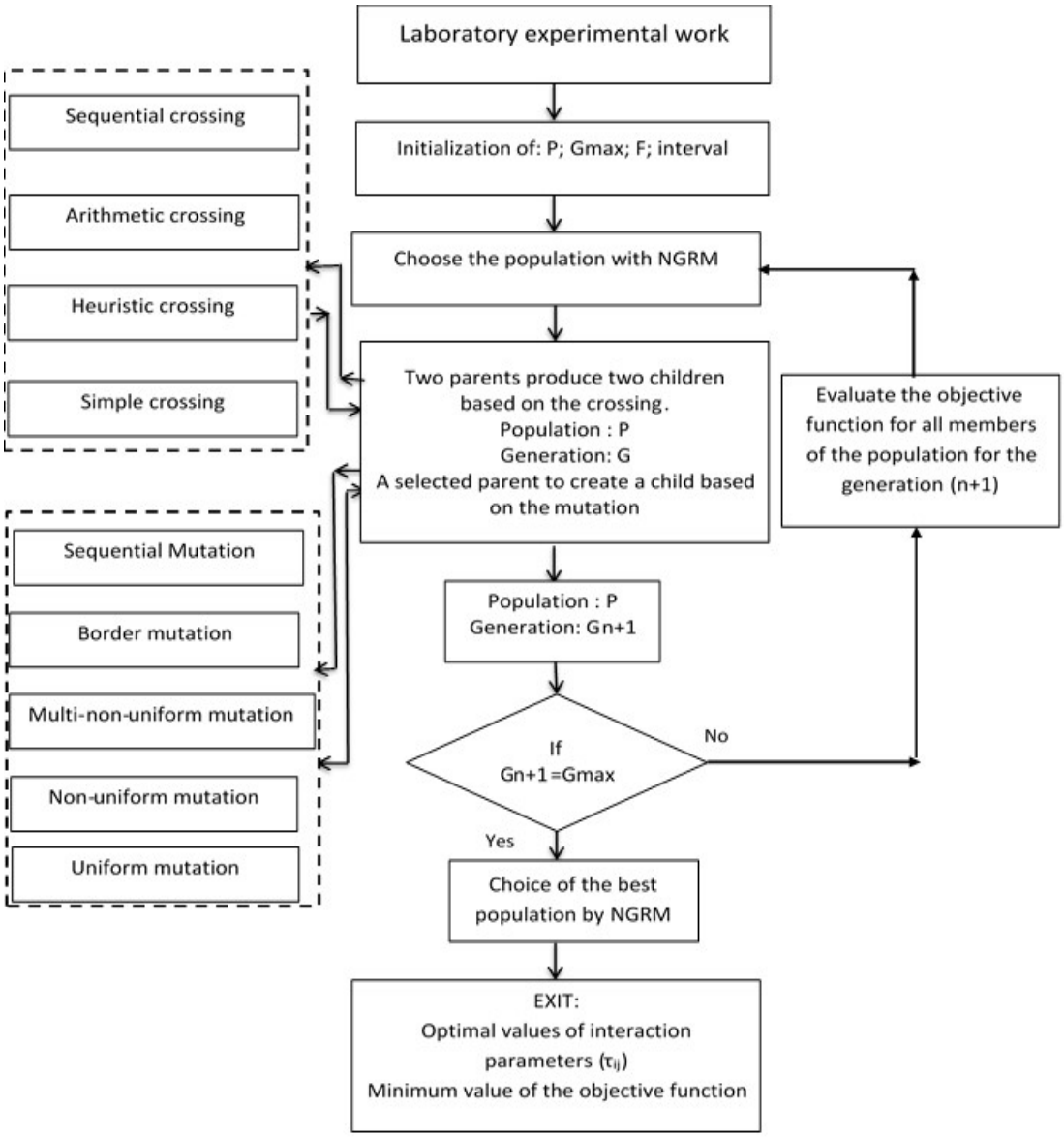

Figure 2. *Flow chart of genetic algorithms [10].*

3.2.3. Analysis

The dosage of the BPA in each phase is made by HPLC analysis. This method of dosage was developed and validated using a thermal HPLC system at 40°C, operating in isocratic mode, using ACN/water (55/45, v/v) system as eluting. The injection volume and the time data acquisition are 10 µg/ml and 10 min respectively. The elution rate was 1 ml/min and the detector is set to the wavelength of 226 nm [14]. Data is integrated by using Breeze 2 software. Well-prepared standard solutions with known concentrations of BPA were used to calibrate the apparatus in the interval of interest composition. The compositions of each constituent were determined by extrapolation from the calibration curves shown in Figures 3, 4, and 5.

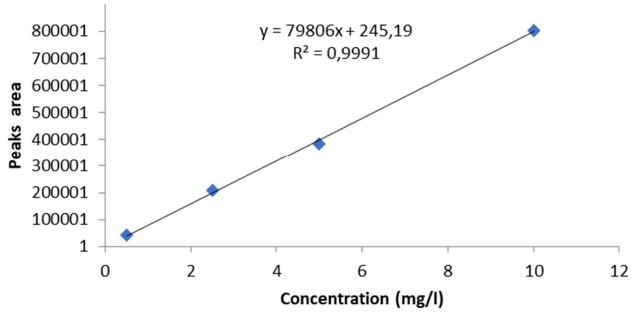

Figure 3. *Calibration curve of BPA in the aqueous phase.*

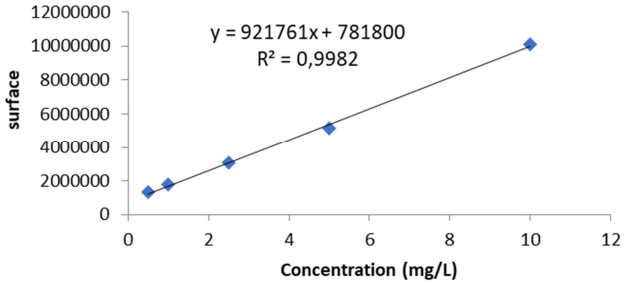

Figure 4. *Calibration curve of BPA in Butan-1-ol.*

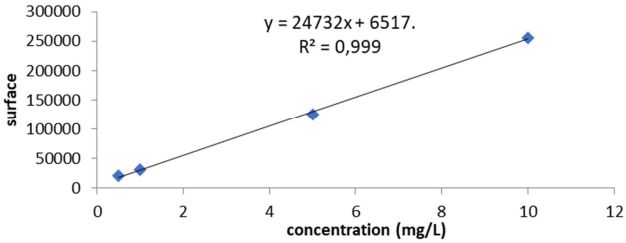

Figure 5. *Calibration curve of BPA in Cyclohexane.*

4. Numerical Method and Sensitivity Analysis

To estimate the interaction parameters of the UNIQUAC and NRTL models, a calculation program on MATLAB based on the method of genetic algorithms has been developed.

Sensitivity analysis is an essential step to condition the quality of the results found. The large number of parameters used for the adjustment of stochastic methods should not make one forget the determination of the values for these parameters. The values of these parameters must not be too disparate depending on the problems addressed. In the literature, intervals of variation of these parameters are determined using tests carried out sequentially. There is no evidence to suggest that the choices made are the best and should be the same for all problems, but they do work. In the present study, the sensitivity analysis carried out makes it possible to fix the values of the critical parameters for adjusting the genetic algorithm [15].

4.1. Genetic Algorithm Setting Parameters

The solution obtained with genetic algorithms depends on a considerable number of parameters, which are among others [15]:

1) The generation maximum number,
2) The population size,
3) The crossing probability,
4) The mutation probability.

The genetic algorithm applied to the liquid-liquid equilibrium of studied systems made it possible here to determine the values of the specific parameters of the genetic algorithm. Thus, the specific parameters of the genetic algorithm determined are the population size and the generation maximum number. Crossing and mutation probabilities are fixed from the literature.

4.1.1. Population Size Effect

In stochastic optimization, the population size choice is very delicate. A too small population will probably evolve towards an unattractive local optimum. A too large population will cause excessive convergence time. The population size must be chosen to achieve a good compromise between the calculation time and the quality of the result. A population size varying between 80 and 100 is reasonable [21, 22].

4.1.2. Maximum Number of Generations

The number of generations is a parameter that makes it possible to avoid getting bogged down in a partial convergence and makes it possible to stop the genetic algorithm when the maximum number is reached. It should be large enough to better visualize the convergence of the solution [15]. The variation of the absolute value of the objective function as a function of the number of generations will make it possible to determine the required number of generations. This variation will be graphically represented.

4.1.3. Crossing Probability

Crossing probability generally depends on the performance function. The higher it is, the more the population will undergo significant changes. In general, this crossing probability is between 0.5 and 0.9 [15].

4.1.4. Mutation Probability

The mutation probability is generally low since a high rate would risk leading the genetic algorithm to a non-optimal solution [15].

4.2. Binary Interaction Parameters Estimation by Genetic Algorithms Technique

The different steps below give the sequences for the determination of interaction parameters by genetic algorithms.

1. Specify the temperature, the number of component Nc, the number of Tie-line k, and the experimental data for each component and each Tie-line.
2. Random generation of chromosomes population (P).
3. Evaluation of each chromosome's objective function.
4. Create a new population by repeating the following steps until the new population is complete:
   a. Selection of two parent chromosomes according to their fitness.
   b. With a given crossing probability, cross two parents to form two new chromosomes (children). If both parents are not crossed; the children are a replica of the parents.
   c. With a given mutation probability mutated new children.
   d. Place the two new children in the population.
5. Use of the new population for the algorithm's next execution.
6. If the stop condition is satisfied, then stop the search and choose the best solution. Otherwise, continue to step 7.
7. Return to step 2.

5. Results and Discussion

5.1. Experimental Result

Table 1. *Linearity of the concentrations space.*

Bisphenol A	Concentration range (mg/L)	Calibration straight line equations	Regression coefficient R^2
Aqueous phase	0.5 - 10	y=79806x + 245.19	0.9991
Organic phase (Butan-1-ol)	0.5 - 10	y=921761x+781800	0.9982
Organic phase (Cyclohexanol)	0.5 - 10	y=139257x-30402	0.9978
Organic phase (Cyclohexane)	0.5 - 10	y=24732x + 6517	0.999

5.2. Experimental Equilibrium Data (Conodals)

The equilibrium data (conodals) for the ternary systems studied are summarized in Table 2 below.

Table 2. *Experimental tie-line data, in mass fraction, in aqueous and organic phases for [Bisphenol A (1) + Water (2) + Solvent (3)].*

Aqueous phase			Organic phase		
X12 (%)	X22 (%)	X32 (%)	X13 (%)	X23 (%)	X33 (%)
Bisphenol A (1) – Water (2) - Butan-1-ol (3)					
16.22	79.46	4.30	87.00	5.74	7.24
16.53	75.14	8.31	79.85	7.02	13.12
16.46	74.15	9.38	76.00	6.86	17.13
16.47	69.06	14.45	69.09	7.36	23.54
16.96	67.24	15.79	63.44	8.19	28.35
Bisphenol A (1) - Water (2) - Cyclohexanol (3)					
11.89	84.33	3.77	78.66	9.01	12.32
12.12	84.10	3.77	77.30	9.03	13.65
12.48	82.14	5.37	76.20	9.33	14.45
12.70	80.05	7.24	74.21	9.18	16.59
12.93	79.82	7.24	70.29	9.40	20.33
Bisphenol A (1) - Water (2) - Cyclohexane (3)					
12.05	83.07	4.87	59.62	10.40	29.97
12.07	81.71	6.21	58.99	10.23	30.77
12.33	80.11	7.54	57.36	9.99	32.64
12.49	78.89	8.61	56.76	10.32	32.91
13.24	75.47	11.28	47.00	15.00	38.00

5.3. Theoretical Results

5.3.1. Liquid-Liquid Equilibrium Modeling and Interaction Parameters Calculation

This second part of the present work displays the different results, which are obtained using the two thermodynamic models UNIQUAC and NRTL. These two models are coupled with a genetic algorithm to determine the interaction parameters of the ternary systems studied. The use of UNIQUAC and NRTL models to predict equilibrium in a solvent mixture requires the prior determination of structural parameters. For the UNIQUAC model, there are structural parameters of volume (R) and structural parameters of surface (Q). For the NRTL model, there are structural parameters called "non-randomness parameters" (α_{ij}). The parameters (R) and (Q) for the UNIQUAC model calculation come from the literature, more precisely from the collection of DECHEMA thermodynamic books [20]. The values of these parameters for various compounds, with a temperature varying from 20°C to 40°C, are grouped in table 3 below.

Table 3. *The structural parameters of the pure components for the UNIQUAC model [20].*

Pure components	R	Q
Butan-1-ol	3.4543	3.052
Cyclohexane	4.0464	3.240
Cyclohexanol	4.3489	3.512
Water	0.9200	1.400
Bisphenol A	9.1266	6.9800

5.3.2. Liquid-Liquid Phases Equilibrium Calculation

The optimization method by the genetic algorithms presented previously is applied for the prediction of equilibrium data. This technique thus makes it possible to estimate interaction parameters of different studied systems.

(i). Population Size Effect

Thus, the minimization of the objective function (equation 3) using a genetic algorithm for each range (interval) was carried out. The effect of the population size on the convergence of the algorithm to optimal values of interaction parameters for the two thermodynamic models (NRTL and

UNIQUAC) is shown in Figures 6 and 7.

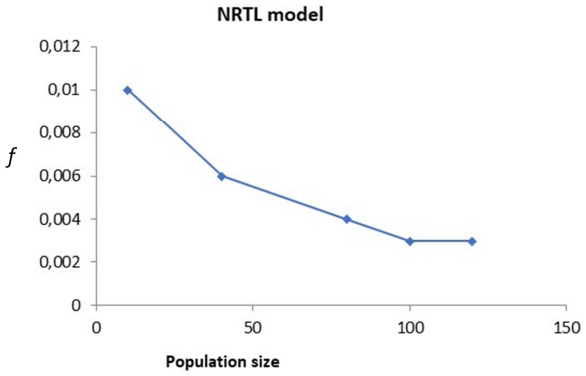

Figure 6. *Effect of population size on objective function for the NRTL model.*

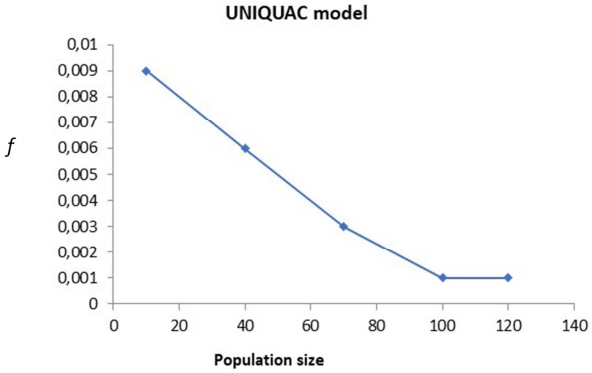

Figure 7. *Effect of population size on objective function for the UNIQUAC model.*

Figures 6 and 7 show that the population size of 100 is good enough to give the right set of interaction parameters for both models. Therefore, during the optimizations of the two models the population size used was 100.

(ii). Generation Maximum Number

Variation of the absolute value of the objective function as a function of the number of generations is shown in Figures 8 and 9. It emerges from the analysis of the curves that the 200th generation is sufficient to give a set of optimum parameters. Therefore, during the optimization of the two models the generation value used was 200.

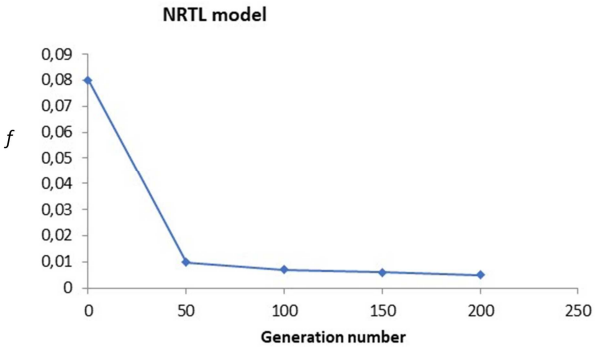

Figure 8. *Effect of generation number on objective function for the NRTL model.*

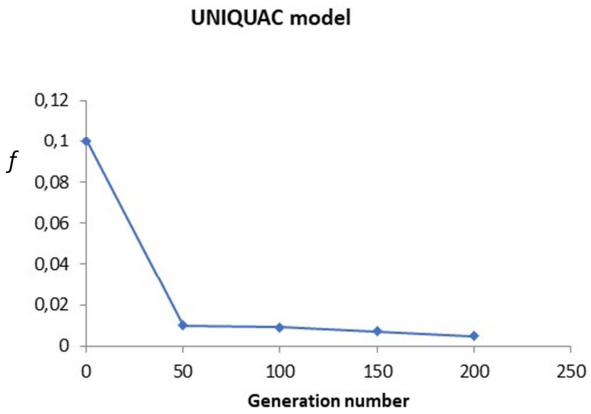

Figure 9. *Effect of generation number on objective function for the UNIQUAC model.*

In summary, after the minimization of the objective function using the genetic algorithm, the values of the specific parameters retained are:

1) the search space size: [-1000, +2000],
2) the population size: 100,
3) the generation maximum number: 200,
4) the mutation probability: 0.01,
5) the crossing probability: 0.8,
6) the selection probability: 0.08.

The genetic algorithm setting values parameters obtained above are in perfect agreement with those of [16]. It is also noted that all the results of calculations carried out are based on the selection method by rank "ranking". The choice of this technique is because several researchers [16 -18] have used this method for the determination of interaction parameters. All the results obtained show that the method of selection by the rank technique is the best.

5.3.3. Model Optimization Results

To calculate the interaction parameters of NRTL and UNIQUAC models, a calculation program on MATLAB software based on the genetic algorithms (GA) method was developed. The results obtained after the optimizations with this MATLAB program; will be analyzed and compared below with those obtained during the experimental phase.

(i). Comparison Between Experimental and Predictive Equilibrium Data

Experimental results described in the previous section are used to calculate the interaction parameters of NRTL and UNIQUAC models in each phase. These interaction parameters are used to calculate the solubility of each constituent in each phase at a constant temperature. Experimental equilibrium data correlation results for the ternary systems (Bisphenol A –Water –Butan-1-ol), (Bisphenol A – Water –Cyclohexanol), and (Bisphenol A – Water –Cyclohexane) are presented below and compared with those from the experimental study. There is a very good agreement between calculated and experimental results, as shown in the analysis of Tables 4 and 5 as well as Figures 10 to 15. These results demonstrate the reliability of the interaction parameters estimated by the genetic algorithm method. These

results also show the ability of the NRTL and UNIQUAC models to make process design and simulation more reliable.

Ternary Diagrams for UNIQUAC Model

Table 4. *Comparison between experimental and predictive equilibrium data (UNIQUAC).*

AQUEOUS PHASE						**ORGANIC PHASE**					
Experimental			**UNIQUAC**			**Experimental**			**UNIQUAC**		
X12	**X22**	**X32**	**X'12**	**X'22**	**X'32**	**X12**	**X22**	**X32**	**X"12**	**X"22**	**X"32**
(Bisphenol A (1) – Water (2) – Butan-1-ol 3))											
0.1622	0.7946	0.0430	0.1605	0.7909	0.0484	0.8700	0.0574	0.0724	0.8709	0.0585	0.0726
0.1653	0.7514	0.0831	0.6451	0.7487	0.0937	0.7985	0.0702	0.1312	0.7995	0.0691	0.1322
0.1646	0.7515	0.0938	0.1585	0.7493	0.1018	0.7600	0.0686	0.1713	0.7590	0.0676	0.1733
0.1647	0.6906	0.1445	0.1638	0.6890	0.1470	0.6909	0.0736	0.2354	0.6900	0.0690	0.2409
0.1696	0.6724	0.1579	0.1673	0.6701	0.1625	0.6344	0.0819	0.2835	0.633	0.0829	0.2839
(Bisphenol A (1) – Water (2) – Cyclohexanol (3))											
0.1189	0.8433	0.0377	0.1187	0.8213	0.0382	0.7866	0.0901	0.1232	0.7867	0.0901	0.1231
0.1212	0.8410	0.0377	0.1207	0.8394	0.0287	0.7730	0.0903	0.1365	0.7731	0.0902	0.1355
0.1248	0.8214	0.0537	0.1218	0.8033	0.0558	0.7620	0.0933	0.1445	0.7622	0.0933	0.1435
0.1270	0.8005	0.0724	0.1296	0.7868	0.0835	0.7421	0.0918	0.1659	0.7407	0.0930	0.1639
0.1293	0.7982	0.0724	0.1352	0.7907	0.0741	0.7029	0.0940	0.2033	0.7039	0.095	0.2011
(Bisphenol A (1) – Water (2) – Cyclohexane (3))											
0.1205	0.8307	0.0487	0.1371	0.8250	0.0441	0.5962	0.1040	0.2997	0.5992	0.1094	0.2913
0.1207	0.8171	0.0621	0.1367	0.8025	0.0606	0.5899	0.1023	0.3077	0.5730	0.1164	0.3105
0.1233	0.8011	0.0754	0.1389	0.7919	0.0771	0.5736	0.0999	0.3264	0.5760	0.1051	0.3187
0.1249	0.7889	0.0861	0.1280	0.7701	0.10018	0.5676	0.1032	0.3291	0.5579	0.1013	0.3407
0.1324	0.7547	0.1128	0.1266	0.7687	0.1045	0.4700	0.1500	0.3800	0.4884	0.1460	0.3654

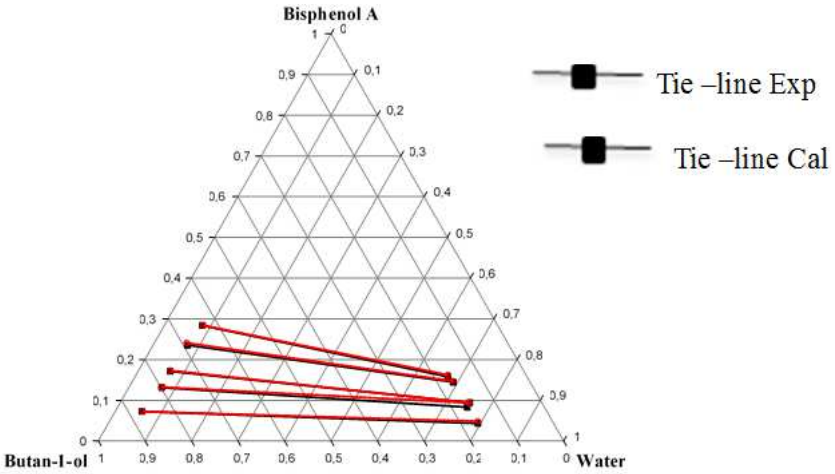

Figure 10. *Ternary diagram of Liquid-liquid equilibrium (Bisphenol A –Water –Butan-1-ol) (3) system for the UNIQUAC model.*

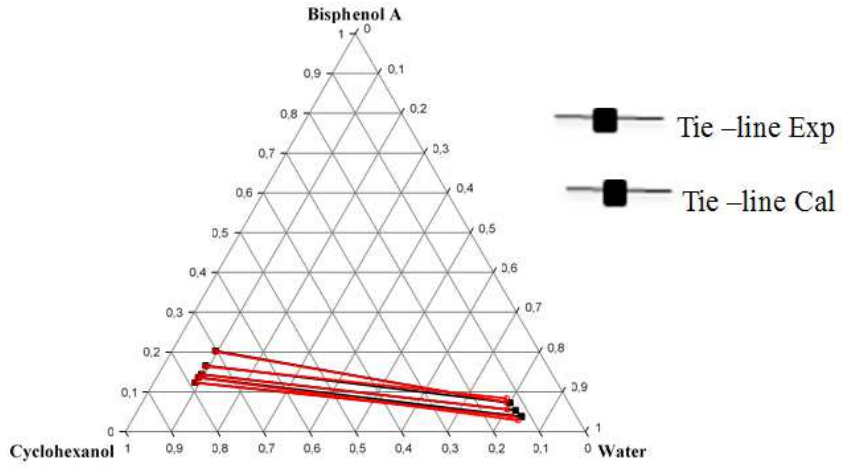

Figure 11. *Ternary diagram of Liquid-liquid equilibrium (Bisphenol A –Water – Cyclohexanol) (3) system for the UNIQUAC model.*

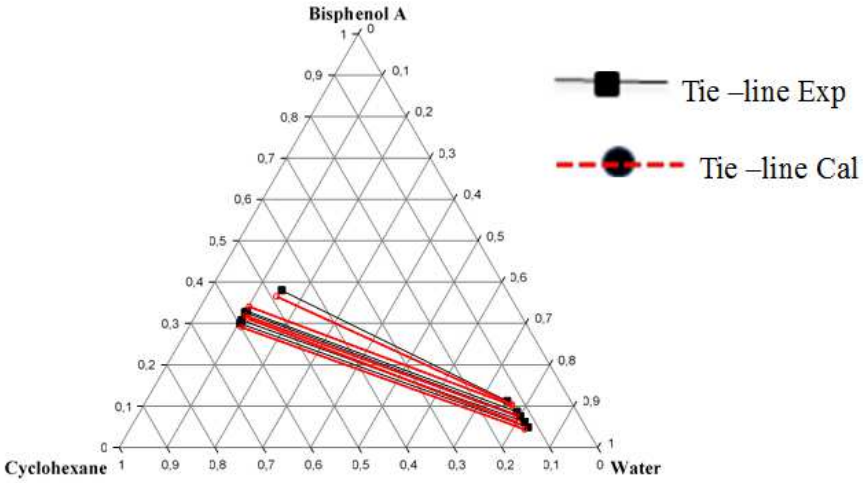

Figure 12. *Ternary diagram of Liquid-liquid equilibrium (Bisphenol A –Water – Cyclohexane) (3) system for the UNIQUAC model.*

Ternary Diagrams for NRTL Model

Table 5. *Comparison between experimental and predictive equilibrium data (NRTL).*

AQUEOUS PHASE						**ORGANIC PHASE**					
Experimental			**NRTL**			**Experimental**			**NRTL**		
X12	**X22**	**X32**	**X'12**	**X'22**	**X'32**	**X12**	**X22**	**X32**	**X"12**	**X"22**	**X"32**
(Bisphenol A (1)–Water (2)–Butan-1-ol 3))											
0.1622	0.7946	0.0430	0.174	0.7877	0.0381	0.8700	0.0574	0.0724	0.8690	0.0544	0.0755
0.1653	0.7514	0.0831	0.1735	0.7462	0.0801	0.7985	0.0702	0.1312	0.7979	0.0669	0.1339
0.1646	0.7515	0.0938	0.167	0.7474	0.0922	0.7600	0.0686	0.1713	0.7591	0.0658	0.1676
0.1647	0.6906	0.1445	0.1657	0.6863	0.1478	0.6909	0.0736	0.2354	0.6953	0.0717	0.2319
0.1696	0.6724	0.1579	0.1739	0.6703	0.1557	0.6344	0.0819	0.2835	0.6330	0.0809	0.2800
(Bisphenol A (1) – Water (2) –Cyclohexanol (3))											
0.1189	0.8433	0.0377	0.1181	0.8355	0.0463	0.7866	0.0901	0.1232	0.9216	0.1049	0.0949
0.1212	0.8410	0.0377	0.1215	0.8338	0.0446	0.7730	0.0903	0.1365	0.7869	0.1069	0.106
0.1248	0.8214	0.0537	0.0888	0.7854	0.0911	0.7620	0.0933	0.1445	0.7670	0.0983	0.1045
0.1270	0.8005	0.0724	0.1362	0.7723	0.0914	0.7421	0.0918	0.1659	0.7472	0.1225	0.1301
0.1293	0.7982	0.0724	0.1602	0.7922	0.0475	0.7029	0.0940	0.2033	0.7042	0.1278	0.1682
(Bisphenol A (1)–Water (2)–Cyclohexane (3))											
0.1205	0.8307	0.0487	0.1303	0.8199	0.0496	0.5962	0.1040	0.2997	0.5897	0.1189	0.2913
0.1207	0.8171	0.0621	0.1350	0.7960	0.0688	0.5899	0.1023	0.3077	0.5771	0.1205	0.3022
0.1233	0.8011	0.0754	0.1386	0.7759	0.0853	0.5736	0.0999	0.3264	0.5699	0.1085	0.3215
0.1249	0.7889	0.0861	0.1304	0.7677	0.1018	0.5676	0.1032	0.3291	0.5582	0.1064	0.3352
0.1324	0.7547	0.1128	0.1402	0.7442	0.1155	0.4700	0.1500	0.3800	0.4567	0.1476	0.3956

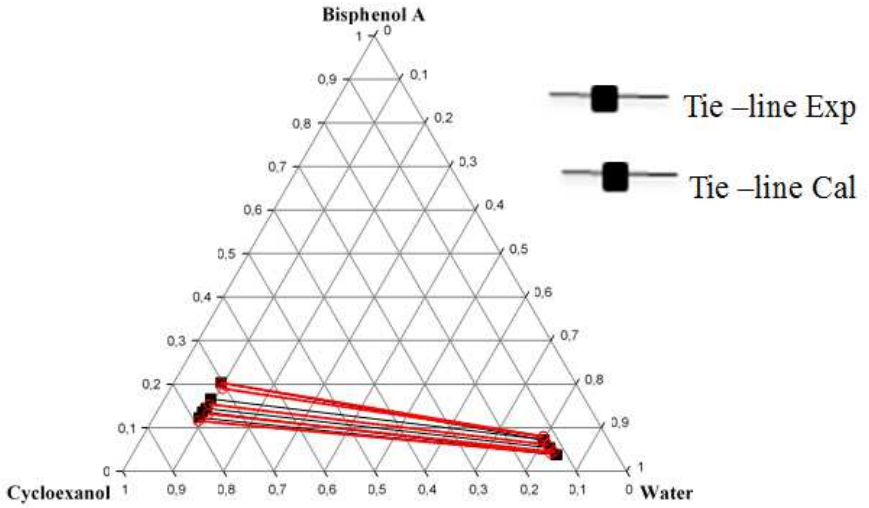

Figure 13. *Ternary diagram of Liquid-liquid equilibrium (Bisphenol A –Water –Butan-1-ol) (3) system for the NRTL model.*

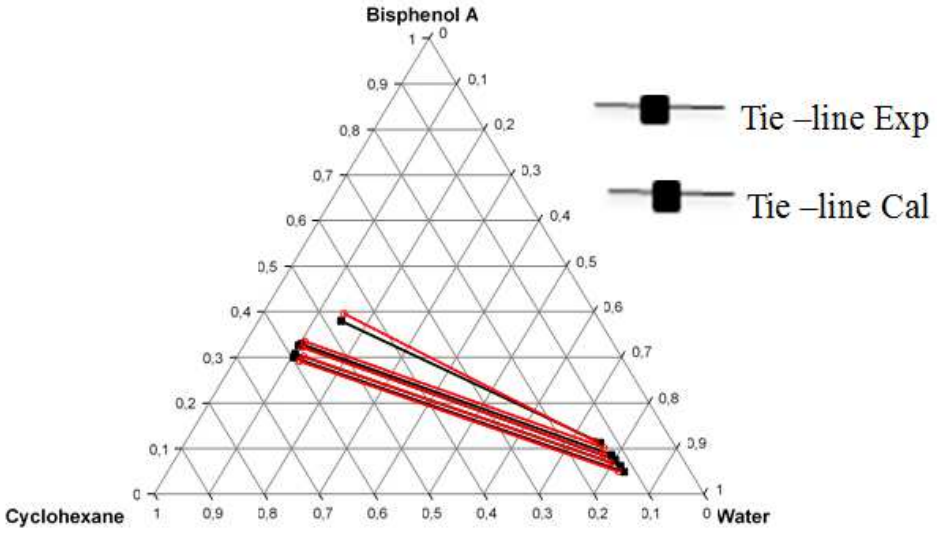

Figure 14. *Ternary diagram of Liquid-liquid equilibrium (Bisphenol A – Water – Cyclohexanol) (3) system for the NRTL model.*

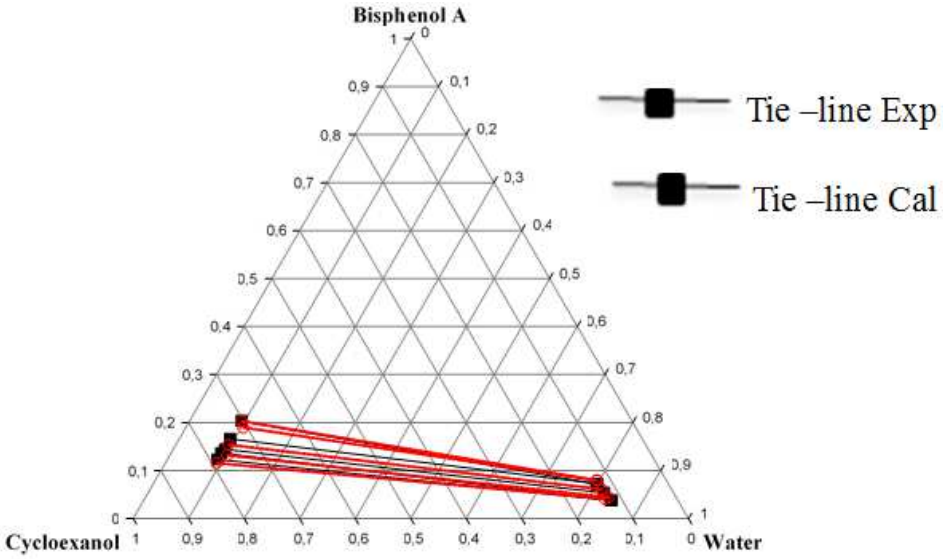

Figure 15. *Ternary diagram of Liquid-liquid equilibrium (Bisphenol A –Water – Cyclohexane) (3) system for the NRTL model.*

(ii). RMSD Values and Interaction Parameters Obtained for Different Ternary Systems

The RMSD values used for the optimization method of the genetic algorithm are presented in Table 6. These values in table 6, present the performance of the algorithm for predicting liquid-liquid phase equilibrium as well as the estimation of interaction parameters of NRTL and UNIQUAC models. Analysis of the results also shows that the RMSD values obtained using the genetic algorithm for the UNIQUAC model are lower than those obtained for the NRTL.

Table 6. *RMSD values for different techniques and thermodynamic models of the ternary systems studied.*

Thermodynamic model studied	Ternary systems	RMSD values
UNIQUAC	Bisphenol A (1) - Water (2) - Butan-1-ol (3)	0.0050
	Bisphenol A (1) - Water (2)- Cyclohexanol (3)	0.0102
	Bisphenol A (1)- Water (2)- Cyclohexane (3)	0.0420
NRTL	Bisphenol A (1) - Water (2)- Butan-1-ol (3)	0.0091
	Bisphenol A (1) - Water (2)- Cyclohexanol (3)	0.0247
	Bisphenol A (1) - Water (2)- Cyclohexane (3)	0.0533

The best (optimal) interaction parameter values obtained for the different systems studied, and the RMSD values are grouped in Tables 7 and 8.

Table 7. *Interaction parameter values Aij and Aji (cal/mol) and RMSD values of the ternary systems studied (UNIQUAC).*

TERNARY SYSTEM	i-j	Aij	Aji	RMSD values
	1-2	-198.49	477.53	
Bisphenol A (1) - Water (2) - Butan-1-ol (3)	1-3	457.87	322.84	0.0018
	2-3	1546.53	-689.42	
	1-2	-725.79	849.50	
Bisphenol A (1) - Water (2)- Cyclohexanol (3)	1-3	-417.74	1742.27	0.0032
	2-3	1490.87	-1219.13	
	1-2	1665.09	479.10	
Bisphenol A (1) - Water (2)- Cyclohexane (3)	1-3	1021.77	1508.72	0.0043
	2-3	1663.96	-551.12	

Table 8. *Interaction parameter values Aij and Aji (cal/mol) and RMSD values of the ternary systems studied (NRTL) (α= 0,2).*

TERNARY SYSTEM	i-j	Aij	Aji	RMSD values
	1-2	-1590.29	521.01	
Bisphenol A (1) - Water (2) - Butan-1-ol (3)	1-3	-1617.27	824.74	0.006
	2-3	1983.77	-940.39	
	1-2	-1856.42	169.04	
Bisphenol A (1) - Water (2)- Cyclohexanol (3)	1-3	-1736.25	1439.34	0.0032
	2-3	1439.25	1118.35	
	1-2	952.37	-598.19	
Bisphenol A (1) - Water (2)- Cyclohexane (3)	1-3	808.24	1874.21	0.0039
	2-3	-950.59	-19.61	

6. Conclusion

This study made it possible to determine the liquid-liquid equilibrium parameters of UNIQUAC and NRTL thermodynamic models for three ternary systems. These three ternary systems are: {Bisphenol A (1) - Water (2)- Butan-1-ol (3)}, {Bisphenol A (1) - Water (2)- Cyclohexanol (3)} and {Bisphenol A (1)- Water (2)- Cyclohexane (3)}. Liquid-liquid equilibrium parameters were determined through the use of the genetic algorithm method implemented in MATLAB software. In this study, two activity coefficient models, UNIQUAC and NRTL were also used to successfully calculate the interaction coefficients. Here again, the genetic algorithm technique was used to estimate the interaction parameters of the studied systems for liquid-liquid extraction. The judicious choice of the genetic algorithm setting values is recommended to determine the optimal interaction parameters. During this present study these recommended values calculated are:

1) the search space size: [-1000, +2000],
2) the population size: 100,
3) the generation maximum number: 200,
4) the mutation probability: 0.01,
5) the crossing probability: 0.8,
6) the selection probability: 0.08.

The results obtained from the resolution of thermodynamic models by the method of genetic algorithms show a very good agreement with the experimental data. It then becomes clear that the method of genetic algorithms is a very reliable technique for the design, modeling, and simulation of processes. Thus, the genetic algorithms technique can therefore be applied to predict liquid-liquid equilibrium and binary interaction parameters for ternary systems {Bisphenol A (1) - Water (2)- Organic Solvent (3)}.

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