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# Application of Genetic Algorithm to the calculation of parameters for NRTL and Two-Suffix Margules models in ternary extraction ionic liquid systems

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ABSTRACT

The stochastic global optimization methods have been extensively used in the fluid phase equilibrium calculations. Among these methods, Genetic Algorithm (GA) can be applied to calculate fitting parameters of activity coefficient models in equilibrium systems. In the present work, based on the GA method, the parameters of NRTL and Two-Suffix Margules models have been calculated for 20 ternary extraction systems containing ionic liquids. The values of the parameters of these models along with the root mean square deviations (rmsd) are reported. The obtained results, in terms of rmsd for these models are satisfactory, with the overall values of 0.0039 and 0.0195 for 169 tie-lines for NRTL and Two-Suffix Margules models, respectively.



## 1. Introduction

In the phase equilibrium calculations, one of the most important problems is the estimation of adjustable parameters in various activity coefficient models. Each model requires a series of parameters which correlate the experimental data while their estimation is a common challenging problem. Concerning phase equilibrium calculations, many different methods have been suggested in the literature. Most of the existing methods for solving phase equilibrium problems are local in nature, generally based on least square objective function or maximization likelihood criterion [1]. In these problems the objective function is highly nonlinear complex expression containing several extremum points within the specified bounds of the variables [2]. Therefore, it is necessary to apply a technique that results in the global optimization of the variables. Some new optimization techniques such as Evolutionary Algorithms including Genetic Algorithm, GA [3], Simulated Annealing, SA [4] and Differential Evolution, DE [5] have been suggested based on the global optimization methods. In recent years, Singh et al. [6] utilized GA to estimate the binary interaction parameters for NRTL and UNIQUAC models in multicomponent LLE systems and demonstrated that their performance was better than inside variance estimation method (IVEM) and the techniques applied in ASPEN and DECHEMA. Sahoo et al. [2,7] calculated the interaction parameters for NRTL and UNIQUAC models in ternary, quaternary and quinary LLE systems based on GA and showed that the results obtained using GA were better than other techniques in literature. Rashtchian et al. [8] studied the phase behavior of multicomponent and multiphase systems based on GA and calculated the binary interaction parameters of Wilson, NRTL and the UNIQUAC models for a number of systems, and compared the binary interaction parameters for these models in VLE, VLLE and LLE systems with those reported in the literature. The results of this comparison showed very good predictions. Alvarez et al. [9] mentioned that stochastic optimization techniques had often been found to be as powerful and effective as deterministic methods in many engineering applications and used GA for parameter estimation in Wilson model for VLE systems. Despite SA needs start points, GA and DE do not require initial guess and just the lower and upper bounds of the variables are required.

Ionic liquids (ILs) are liquid salts at room temperature. They are usually composed of large asymmetric organic cations and inorganic or organic anions. Most commonly considered for extraction and synthesis are those with cations based on the imidazolium or pyridinium ring with one or more alkyl groups attached to the nitrogen or carbon atoms [10]. In recent years, they have attracted considerable attention for their potential as "designer solvents". Due to their negligible vapor pressure and electrolyte properties, they can be applied as replacements for conventional toxic, flammable and volatile organic solvents, and become very interesting

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**Table 1**
Abbreviation and full name of ionic liquids used in this work.

| Abbreviation | Full name of ionic liquid |
|---|---|
| [mebupy][$BF_4$] | 4-Methyl-N-butylpyridinium tetrafluoroborate |
| [3-mebupy][DCA] | 3-Methyl-N-butyl pyridinium dicyanamide |
| [emim][$ESO_4$] | 1-Ethyl-3-methylimidazolium ethylsulfate |
| [bmim][$MSO_4$] | 1-Butyl-3-methylimidazolium methylsulfate |
| [bmim][$BF_4$] | 1-Butyl-3-methylimidazolium tetrafluoroborate |
| [bmim][$NTf_2$] | 1-Butyl-3-methylimidazolium bis{trifluoromethylsulfonyl}imide |
| [bmim][$PF_6$] | 1-Butyl-3-methylimidazolium hexafluorophosphate |
| [omim][CL] | 1-Octyl-3-methylimidazolium chloride |
| [hmim][$BF_4$] | 1-Hexyl-3-methylimidazolium tetrafluoroborate |
| [pmim][$PF_6$] | 1-Propyl-3-methylimidazolium hexafluorophosphate |
| Ammoeng 102 | Tetraalkyl ammonium sulfate |
| [bmim][SCN] | 1-Butyl-3-methylimidazolium thiocyanate |
| [bpy][$BF_4$] | N-Butylpyridinium tetrafluoroborate |
| [EtMe][$ImI_3$] | 1-Ethyl-3-methylimidazolium triiodide |
| [bmim][DCA] | 1-Butyl-3-methylimidazolium dicyanamide |
| [hmim][TCB] | 1-Hexyl-3-methylimidazolium tetracyanoborate |
| [bmim][TCB] | 1-Butyl-3-methylimidazolium tetracyanoborate |
| [omim][$PF_6$] | 1-Octyl-3-methylimidazolium hexafluorophosphate |
| $C_2NTf_2$ | Ethyl(2-hydroxyethyl)dimethylammonium bis{(trifluoromethyl)sulfonyl}imide |
| [dmim][MP] | 1,3-Dimethylimidazolium methylphosphonate |

entrainers in separation processes (e.g., extractive distillation, liquid–liquid extraction, absorption) [11]. Nowadays, they are known as green solvents for future applications. Over the past few years, research about ILs has been increased greatly due to their unique specifications. Although an increasing amount of experimental phase equilibrium data of binary and ternary mixtures containing ILs is becoming available, it is important to be able to predict the phase equilibrium in such mixtures.

In the present work, for calculation of parameters in NRTL and Two-Suffix Margules models, LLE data for 20 ternary extraction systems including 20 different ILs have been used. The values of the parameters for the models along with the root mean square deviations (rmsd) are reported. Comparison of the results obtained using GA with other methods based on local optimization, e.g. least square method, shows that GA is reliable algorithm in parameter estimation problems. The rmsd results show that mentioned models can correlate the experimental data of ternary extraction systems including ILs. The full names and abbreviations for the ILs used in this work are presented in Table 1.

## 2. Genetic Algorithm

In the recent years, Genetic Algorithm (GA) has been found to be a reliable algorithm for the complex engineering calculations. GA is based on the natural selection and the process that drives biological evolution. Those optimization problems that are not well suited for standard optimization algorithms, including problems in which the objective function is discontinuous, non-differentiable stochastic or highly nonlinear can be solved by GA. GA differs from a derivative-based optimization algorithm in two main ways. Firstly, the derivative-based algorithm uses only one single point in each iteration, while GA explores the search space using multiple points. Secondly, the derivative-based algorithm generates new point by a deterministic computation, while GA creates new population by a probabilistic computation. The fitness function is the function that is requested for optimization. For standard optimization algorithm, this is known as the objective function. The algorithm begins by creating random initial populations and modifies a population of individual solutions between the values of lower and upper bounds of variables successively. The population size determines the size of population at each generation. Increasing the population size enables GA search more points and thereby obtaining better results. At each step, GA selects individuals from the current population stochastically to be the parents of the children for the next generation based on genetic operators including selection, crossover and mutation by exploring all regions of the search space. The procedure of GA is summarized in Fig. 1. In the first step, an initial population is generated. Each individual is evaluated for fitness in the next step. The best individuals are chosen from the selection step. Individuals with high probability receive more probability to produce offspring. The offspring are then generated by combination of these selected individuals using crossover step. In mutation step, random changes are applied to some individuals. The purpose of mutation operator is to prevent GA from converging to a local minimum and introducing new possible solutions into the population [12]. The algorithm continues to find the minimum of the fitness function and evaluated until termination criteria are reached. The most frequently used stopping criterion is specified maximum number of generations. A more complete discussion of GA, including extension and related topics, can be found in the Genetic Algorithm and Direct Search toolbox users guide [13].

## 3. Liquid–liquid equilibrium modeling

Thermodynamic equilibrium condition between two liquid phases, i.e. the aliphatic rich phase I and the IL rich phase II, in terms of the molar fractions $x_i$ and activity coefficients $\gamma_i$, can be expressed in the following form:

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \quad (1)$$

The molar component balances lead to the following equation:

$$Z_i = x_i^{\mathrm{I}}L + x_i^{\mathrm{II}}(1-L) \quad (2)$$

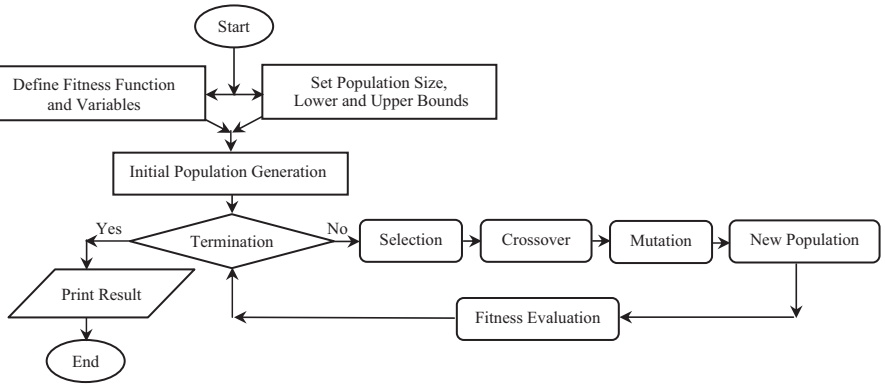


**Fig. 1.** The flowchart of Genetic Algorithm toolbox.