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Optimization of Process Design Problems Using Differential Evolution Algorithm

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Abstract: A modified differential evolution algorithm (MDE) has been used for solving different process related design problems (namely calculation of the NRTL and Two-Suffix Margules activity coefficient models parameters in 20 ternary extraction systems including different ionic liquids and reactor network design problem). The obtained results, in terms of root mean square deviations (rmsd) for these models are satisfactory, with the overall values of 0.0023 and 0.0170 for 169 tie-lines for NRTL and Two-Suffix Margules models, respectively. The results showed that the MDE algorithm results in better solutions compared to the previous work based on genetic algorithm (GA) for correlating liquid-liquid equilibrium (LLE) data in these systems. MDE also outperformed DE algorithm when tested on reactor network design problem with respect to convergence and speed.

Keywords: NRTL, Two-suffix margules, Parameter estimation, Ionic liquid, Optimization.

تحقيق الحل الأمثل لمشاكل تصميم العمليات باستخدام منهاج النمو التفاضلي المعدل

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الملخص: تم استخدام منهاج النمو التفاضلي المعدل (MDE) من أجل حل العمليات المختلفة المتعلقة بمشاكل التصميم (أي حساب NRTL ومعامل النشاط لمعطيات النماذج Two-Suffix Margules في ٢٠ نظام استخلاصي ثلاثي بما في ذلك السوائل الأيونية المختلفة ومشكلة تصميم شبكة مفاعليه). النتائج التي تم الحصول عليها، بدلالة انحرافات متوسط الجذر التربيعي (rmsd) لهذه النماذج كانت مرضية، مع قيم إجمالية ٠,٠٠٢٣ و٠,٠١٧٠ لعدد ١٦٩ من خطوط الربط NRTL واثنين من لاحقة نماذج Margules، على التوالي. وأظهرت النتائج أن منهاج النمو التفاضلي المعدل ينتج عنه حلول أفضل مقارنة مع الأعمال السابقة المبنية على المنهاج الجيني (GA) عند إيجاد علاقات الربط لبيانات التوازن السائل- السائل (LLE) في هذه الأنظمة. كما تفوق منهاج النمو التفاضلي المعدل (MDE) على منهاج النمو التفاضلي (DE) عند اختباره على مشكلة تصميم شبكة مفاعليه وذلك فيما يتعلق بالوصول للحل وتعجيل هذا الوصول.

الكلمات المفتاحية: النمو التفاضلي المعدل (MDE)، NRTL، margules، تقدير المعطيات، توازن السائل- السائل، السوائل الأيونية ، تصميم شبكة مفاعليه، تحقيق الحل الأمثل.

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Nomenclature

List of symbols

A	interaction parameter
CR	crossover constant
F	Scaling factor
F_{obj}	Objective function
G	Energy parameter
Gmax	maximum number of generations
K	*D*istribution ratio
L	Molar split ratio
M	Number of tie lines
NP	Population size
R	Universal gas constant
T	Absolute temperature
x	Liquid-phase mole fraction
Z	Overall, or make-up molar fraction

Greek letters

γ	activity coefficient
τ	energy parameter
a	non-randomness parameter

Superscript and Subscripts

cal	calculated value
exp	experimental value
I, II	two liquid phases at equilibrium
i, j, k	component, phase and tie line respectively
1, 2, 3	aromatic, aliphatic and ionic liquid respectively

1. Introduction

Phase equilibria play an important role in the synthesis, development, design, and control of chemical and petroleum engineering processes. Phase behavior is often analyzed using equation of state and activity coefficient models. Though lots of data is available in literature which correlate both the model and experimental data, estimation of accurate model parameters still remain a challenge. Local optimization methods (such as Newtons method or least square techniques, etc.) are often used to solve phase equilibrium problems. But because the search space is highly nonlinear consisting of local and global minima's, the local methods may converge to a local optimum point (Stragevitch and Davila 1997; Sahoo *et al*. 2006). In recent past the stochastic optimization techniques (such as differential evolution (DE), genetic algorithms (GA), simulated annealing (SA), particle swarm algorithm, etc.) (Holland 1992; Kirkpatrick *et al*. 1983; Price *et al*. 2005) have shown considerable potential in solving complex engineering problems (such as phase equilibrium problems, reaction engineering problems, process calculations related optimization problems etc.). Liquid-Liquid-Equilibrium (LLE) has remained a very challenging problem for non-ideal liquid solutions such as ionic liquids (ILs). ILs are green solvent and they have shown potential applications in many separation processes (Lei *et al*. 2009). For designing any separation processes using ionic liquids, the accurate estimation of activity coefficient parameters is of vital importance. As a quick review on these problems we may refer to the following works:

GA has been utilized for estimation of the parameters for two well-known activity coefficient models (*ie*. NRTL and UNIQUAC) (Singh *et al*. 2005). They proved that their results were better than local search methods. In another study (Sahoo *et al*. 2006; Sahoo *et al*. 2007), GA was used to estimate ternary, quaternary and quinary LLE interaction parameters for NRTL and UNIQUAC models. It was reported that GA results were better than other techniques. Another group of authors (Rashtchian *et al*. 2007) also used a stochastic method (genetic algorithm) for phase behavior of multiphase and multicomponent systems. They calculated the binary interaction parameters of UNIQUAC, NRTL and Wilson models for a number of systems. They also reported their data and compared their data for various systems (including vapor liquid equilibrium, vapor-liquid-liquid equilibrium, and liquid-liquid equilibrium) form the literature. In some other studies, GA was successfully applied for estimation of interaction parameters of other complex models for systems of LLE containing ionic liquids and also for modeling of viscosity of crude oil binary blends (Vatani *et al*. 2012; Vakili-Nezhaad *et al*. 2013; Vakili-Nezhaad *et al*. 2014; Al-Maamari *et al*. 2015).

Modified DE algorithm is used for calculation of two complex problems. The performance of MDE algorithm is also explored by comparing its output with other algorithms. Parameters of two activation coefficient models (which include NRTL and Two-Suffix-Margules model) are calculated using experimental data having 20 sets of ternary liquid systems having 20 different ILs. The reactor network problem is also solved and both the speed and accuracy aspects of MDE algorithm are reported. The statistical parameters of the models including root mean square deviation for the above mentioned set of ternary systems is reported. Comparison of the results obtained using MDE with our previous work based on GA (Vatani *et al*. 2012) shows that MDE is a very reliable algorithm in parameter estimation problems which can give more accurate results compared to GA. Abbreviation, full names and list of ternary ionic liquid systems used in this study is given in Table 1.

2. Problem formulation

2.1. The LLE Modeling

The LLE modeling is based on thermodynamic equilibrium condition for mole fractions and activity coefficient between the aliphatic rich phase (I) and the IL rich phase (II).

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

The molar component balances lead to the following equation:

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

where x, γ, Z and L are mole fraction, activity coefficient, the overall mole fraction and the molar split ratio respectively, and the subscript i denotes the components.

Considering the distribution ratio of component as below:

$$K_i = \frac{x_i^{\mathrm{I}}}{x_i^{\mathrm{II}}} \tag{3}$$

and solving Eq. (3) with Eq. (2), the Rachford–Rice equation (Seader and Henley 2006) is concluded as:

Table 1. Abbreviation, full name and list of ternary ionic liquid systems used in this work.

Abbreviation	Full name of ionic liquid	Sys. No.	Name of ternary systems	*T* (K)	Tie-line	Ref.
[mebupy][BF_4]	4-methyl-N-butylpyridinium tetrafluoroborate	1	propylbenzene(1)+hexadecane(2)+[mebupy][BF_4](3)	313.00	10	Alkhaldi et al. 2011
[3-mebupy][DCA]	3-methyl-N-butyl pyridiniumdicyanamide	2	benzene(1)+hexane(2)+[3-mebupy][DCA](3)	303.15	11	Hansmeier et al. 2010a
[emim][ESO_4]	1-ethyl-3-methylimidazolium ethylsulfate	3	benzene(1)+hexane(2)+[emim][ESO_4](3)	313.20	08	García et al. 2009
[bmim][MSO_4]	1-butyl-3-methylimidazolium methylsulfate	4	Benzene(1)+Hexane(2)+[bmim][MSO_4](3)	328.20	08	García 2010a
[bmim][BF_4]	1-butyl-3-methylimidazolium tetrafluoroborate	5	Benzene(1)+Heptane(2)+[bmim][BF_4](3)	298.15	08	Revelli et al. 2010
[bmim][NTf_2]	1-butyl-3-methylimidazolium bis{trifluoromethylsulfonyl}imide	6	benzene(1)+octane(2)+[bmim][NTf_2](3)	298.15	13	Domínguez et al. 2011
[bmim][PF_6]	1-butyl-3-methylimidazolium hexafluorophosphate	7	benzene(1)+Undecane(2)+[bmim][PF_6](3)	298.15	05	Maduro and Aznar 2008
[omim][CL]	1-octyl-3-methylimidazolium chloride	8	benzene(1)+Dodecane(2)+ [omim][CL](3)	298.20	04	Letcher and Deenadayalu 2003
[hmim][BF_4]	1-hexyl-3-methylimidazolium tetrafluoroborate	9	benzene(1)+Hexadecane(2)+[hmim][BF_4](3)	298.20	09	Letcher and Reddy 2005
[pmim][PF_6]	1-propyl-3-methylimidazolium hexafluorophosphate	10	benzene(1)+Cyclohexane(2)+[pmim][PF_6](3)	298.15	08	Zhou et al. 2012
Ammoeng 102	tetraalkyl ammonium sulfate	11	toluene(1)+heptane(2)+Ammoeng102(3)	298.15	08	Pereiro and Rodriguez 2009
[bmim][SCN]	1-butyl-3-methylimidazolium thiocyanate	12	Toluene(1)+heptane(2)+[bmim][SCN](3)	303.15	07	Hansmeier et al. 2010b
[bpy][BF_4]	N-butylpyridiniumtetrafluoroborate	13	Toluene(1)+heptane(2)+[bpy][BF_4](3)	313.20	08	García et al. 2010b
[EtMe][ImI_3]	1-ethyl-3-methylimidazolium triiodide	14	Toluene(1)+heptane(2)+[EtMe][ImI_3](3)	318.15	14	Selvan et al. 2000
[bmim][DCA]	1-butyl-3-methylimidazolium dicyanamide	15	Toluene(1)+heptane(2)+[bmim][DCA](3)	328.15	07	Hansmeier et al. 2010b
[hmim][TCB]	1-hexyl-3-methylimidazolium tetracyanoborate	16	toluene(1)+methylcyclohexane(2)+[hmim][TCB](3)	293.15	09	Gutierrez et al. 2011
[bmim][TCB]	1-butyl-3-methylimidazolium tetracyanoborate	17	toluene(1)+methylcyclohexane(2)+[bmim][TCB](3)	313.15	09	Gutierrez et al. 2011
[omim][PF_6]	1-octyl-3-methylimidazolium hexafluorophosphate	18	m-xylene(1)+Nonane(2)+[omim][PF_6](3)	298.15	04	Maduro and Aznar 2010
C_2NTf_2	ethyl(2-hydroxyethyl)dimethylammoniumbis{(trifluomethyl)sulfonyl}imide	19	m-xylene(1)+hexane(2)+[C_2NTf_2](3)	298.15	10	Dománska et al. 2007
[dmim][MP]	1,3-dimethylimidazolium methylphosphonate	20	Thiophene(1)+Heptane(2)+[dmim][MP](3)	298.15	09	Revelli et al. 2010
			Overall		169	

$$\sum_i \frac{Z_i(1-K_i)}{1+L(K_i-1)} = 0 \quad (4)$$

Considering Eq. (1), Eq. (3) can be rewritten as $K_i = \gamma_i^{II} / \gamma_i^{I}$, where γ_i is proper activity coefficient models with an appropriate adjustable parameters.

2.2. *The NRTL and Two-Suffix Margules Models*

In the present work, the experimental LLE data were correlated by NRTL and Two-Suffix Margules models (Renon and Prausnitz 1968; Prausnitz *et al*. 1999). The activity coefficient γ_i of NRTL model is expressed as:

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{m} G_{ki} x_k} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{k=1}^{m} G_{kj} x_k} \left[\tau_{ij} - \frac{\sum_{k=1}^{m} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{m} G_{kj} x_k} \right] \quad (5)$$

where the binary interaction A_{ij}, and non-randomness parameters a_{ij}, have been defined as:

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} = \frac{A_{ij}}{T}, G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (6)$$

so in general A_{ii}= A_{jj}=0, $A_{ij} \neq A_{ji}$ and a_{ij} = a_{ji}.

Beside NRTL model, the activity coefficients of Two-Suffix Margules model are as below:

$$Ln\gamma_1 = A_{12}x_2^2 + A_{13}x_3^2 + (A_{12} + A_{13} - A_{23})x_2x_3 \quad (7)$$

$$Ln\gamma_2 = A_{12}x_1^2 + A_{23}x_3^2 + (A_{12} + A_{23} - A_{13})x_1x_3 \quad (8)$$

$$Ln\gamma_3 = A_{13}x_1^2 + A_{23}x_2^2 + (A_{13} + A_{23} - A_{12})x_1x_2 \quad (9)$$

where, A_{12}, A_{13} and A_{23} are the interaction parameters, which were regressed by ternary systems data used in this work.

2.3. *Objective Function and Decision Variables*

The single objective optimization study is considered. The experimental data for 20 ternary extraction systems containing different ionic liquids are used. NRTL and Two-Suffix Margules activity coefficient models parameters are estimated using the modified differential evolution algorithm. In general, parameter estimation is considered as a minimization of an objective function value (F_{obj}) (Revelli *et al*. 2010), which minimizes the deviation between the experimental and calculated mole fractions of the components. This part of study deals with the estimation of thermodynamic activity coefficient models parameters for a ternary set of systems, accordingly the problem is formulated as:

$$Minimize \quad F_{obj} = \left[\sum_i \sum_j \sum_k \left(x_{i,j,k}^{\exp} - x_{i,j,k}^{cal} \right) \right] \quad (10)$$

Lower and uppers bounds of parameters used in this work are given in Table 2. The criterion for comparison between the experimental and calculated data is given by the following equation.

$$rmsd = \left[\sum_i \sum_j \sum_k (x_{ijk}^{\exp} - x_{ijk}^{cal})^2 / 6M \right]^{1/2} \quad (11)$$

where, x and M are mole fraction and the number of tie lines and subscripts i, j and k are component, phase, and tie lines respectively.

In this study Reactor Network Design (RND) problem is considered for optimization study. RND problem is optimized using variants of differential evolution algorithms namely, DE and MDE.

2.4. *Reactor Network Design Problem:*

This RND design problem is obtained from Ryoo and Sahinidis (Ryoo and Sahinidis 1995) (see Fig. 1). Two CSTR reactors in sequence having consecutive reactions (P→Q→R) are considered. The intermediate product concentration leaving the second reactor is maximized in this problem.

Both the global and local solutions for this problem are reported in literature (Angira 2006; Babu and Angira 2006). The problem is reformulated by removing the equality constraint (Eqs. 12-15):

$$Maximize.\ f = \frac{k_2 x_6 * (1 + k_3 x_5) + k}{{}_1 x_5 * (1 + k_2 x_6)} \Big/ \frac{}{(1 + k_{11} x_5) * (1 + k_{22} x_6) * (1 + k_{13} x_5) * (1 + k_{24} x_6)} \quad (12)$$

$$\text{Sub. to:} \quad x_5^{0.5} + x_6^{0.5} \leq 4 \quad (13)$$

Table 2. Interaction parameters values used in present study for the systems.

Component	NRTL			Margules
i-j	A_{ij}	A_{ji}	a_{ij}	A_{ij}
1–2	[1, 2500]	[-500, 2500]	[0.15, 0.5]	[-10, 50]
1–3	[1, 2500]	[-500, 2500]	[0.15, 0.5]	[-10, 50]
2–3	[1, 2500]	[1, 2500]	[0.15, 0.5]	[-10, 50]

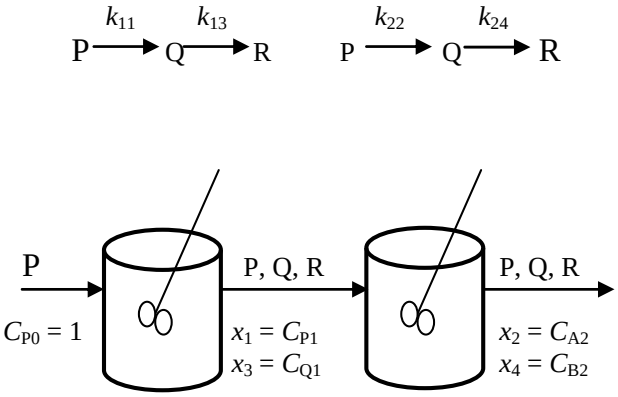

Figure 1. Reactor network design problem.

$$10^{-5} \leq x_5 \leq 16 \quad (14)$$

$$10^{-5} \leq x_6 \leq 16 \quad (15)$$

where, k_{11} =0.09755988, k_{22} =0.99*k_1, k_{13} =0.0391908, k_{24} =0.9*k_3

In this study, DE and MDE algorithms are used to solve the reformulated problem.

3. Modified Differential Evolution (MDE)

The survival of the fittest principle is used in both DE and MDE. Against DE, MDE maintains only one array of variables (bounded by lower and upper bounds). This population gets improved if a better candidate solution is obtained by allowing new solution to take part in the cross over and mutations operations in the same generation. Thus it is observed that number of function evaluations are lowered thus improving the convergence of algorithm. It has been found in the previous studies that an updating the single array continuously enhances the convergence speed leading to less function evaluations as compared to DE (Price *et al*. 2005). MDE also offers advantages of one array consuming less memory and an improvement on CPU time. Premature convergence can be avoided by wisely/appropriately choosing the key parameters of MDE (such as NP, CR and F) (Fan and Lampinen 2003; Angira and Babu 2006). Both DE and MDE algorithms are widely used in the field of non-linear chemical processes, computational magnetics, process synthesis and design problems, and computational fluid dynamics, etc. (Angira and Babu 2006; Angira 2006; Stumberger *et al*. 2000; Colaco *et al*. 2004). Similarly multi-objective optimization strategies of differential algorithms are successfully applied on selected real world optimization problems (such as MOO of LDPE tubular reactor, styrene reactor (both adiabatic and pseudo-isothermal reactor), PTA oxidation process, *etc*.) (Gujarathi and Babu 2009a; Gujarathi and Babu 2009b; Gujarathi and Babu 2010a; Gujarathi and Babu 2010b; Gujarathi and Babu 2011). These MOO strategies of DE algorithms are in general found to outperform some other existing evolutionary strategies of MOO.

4. Results and Discussion

4.1. Effect of Key Parameters (CR, F, and NP)

Modified differential evolution is a population based stochastic type of algorithm. It is observed that the outcome of stochastic algorithms, in general, depends on its control parameters. The performance of DE and MDE algorithms depends on key parameters, namely, NP, CR, and F. Three systems (System 1, 6 and

10) are selected randomly. Table 3 shows the parameter values used in this study. All the optimization runs were run for 150 numbers of generations. Various optimization runs are carried out by judiciously varying these control parameters for each of the selected systems. Population size is plotted versus objective function and is shown through Fig. 2a. There is no fixed guideline about the optimum size of population. If the population size is too low, it becomes difficult for an algorithm to converge

Table 3. Parameter values used in present study.

Parameter	Value
Population size (NP)	120
Maximum Number of generations (Gmax)	150
Crossover constant (CR)	0.8
Scaling Factor (F)	Random (0,1)

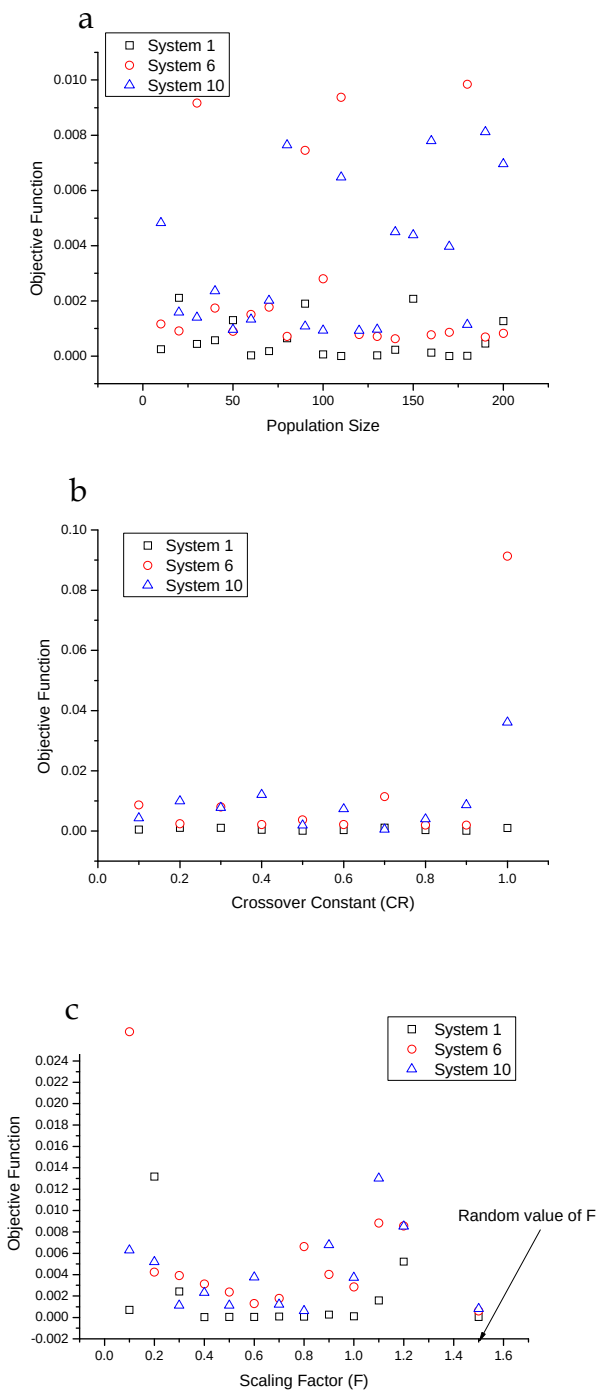

Figure 2. Effects of control parameters a) Population size; b) Crossover constant; and c) Scaling factor.

optimally. The computation cost increases by increasing the population size. In this optimization study, population specific runs are carried out by varying the population size for each system. Results for three randomly selected systems are plotted and shown in Fig. 2a. Accordingly population size of 120 is selected and is used during the optimization study in this work. Similarly the crossover constant and the scaling factors are also varied and results for three randomly selected systems are shown in Fig. 2b, and Fig. 2c. Similar results could be obtained for all systems in this work.

4.2. *Comparison of MDE, GA and other Methods from Literature*

The MDE algorithm is used to calculate the interaction parameters of NRTL and Two-Suffix Margules activity coefficient models in LLE systems shown in Table 1. Both the optimization and model simulation codes are written and simulated using MATLAB (2009) software. During optimization study, three systems are randomly selected to study the effects of parameters on objective function. The objective function value with respect to generation number is plotted for 3 randomly selected systems. Fig. 3 shows that irrespective of selected system (in this study); the MDE algorithm converges to the minimum function value in less than 90 generations. However, the algorithm is allowed to run for 150 numbers of generations to ensure that the optimum is reached.

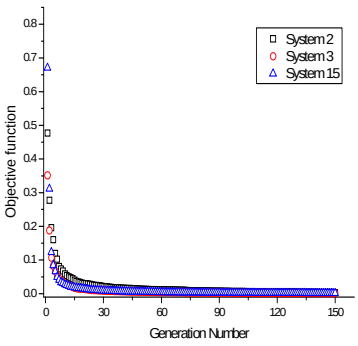

Figure 3. Convergence profile of selected systems using MDE.

Population based stochastic algorithms have a typical feature that they start with population of points and all the points are expected to converge to the optimum points. The results are shown through Table 4 and Table 5. Table 4 shows the calculated parameters of the individual models for each individual system. Table 5 shows the results of rmsd obtained using MDE and GA and other methods form literature. MDE is able to converge to the global optimum having overall rmsd values of 0.0023 and 0.0170 for NRTL and Two-Suffix Margules models. As an example, the experimental and calculated tie-lines were compared in Figs. 4 and 5 for the system No.1.

4.3. *Optimization of CSTR Reactor Design Network*

Table 6 shows the results obtained using DE and MDE for the optimization of reactor network design problem. Results are shown considering average best, worst, mean, median, and standard deviation of the optimum values of 25 runs. Though the experimental runs are taken for 500 numbers of generations, the comparison of results is carried out at intermediate numbers of functions evaluations (FES) *ie*. FES value of 10000, 15000, 20000, 50000 and 100000 (Corresponding to 50, 75, 100, 250 and 500 generations respectively). Taking standard deviation to be one of the measures of the effectiveness of any algorithm, it is observed that MDE produces better results than those obtained using DE. The consistency with which DE and MDE has performed is evident from the fact that standard deviation achieved a value of 0 (zero) or close to zero. Figure 6 shows that error reduces faster in MDE compared to DE. Table 7 shows FES, CPU time and function value for various problems using strategies of DE. MDE algorithm finds the global optimum in lesser number of FES than DE. The CPU time taken by MDE is much lesser compared to DE.

5. Conclusion

Binary interaction parameters of two well-known activity coefficient models are calculated for 20 different extraction systems having ILS based on flash systems using Modified DE and genetic algorithms. The activity coefficient models parameters as well as the rmsd have been obtained and are reported. The MDE algorithm successfully converged to the global optimum having rmsd value of 0.0023 and 0.0170 for NRTL and Two-Suffix Margules models respectively for 169 tie-lines. The NRTL

Table 4. The calculated parameters of NRTL and Two-Suffix Margules models for ternary systems listed in Table 1.

Sys. No	Com. *i-j*	Genetic Algorithm				Differential Evolution (Present study)			
		NRTL			Margules	NRTL			Margules
		A_{ij}	A_{ji}	a_{ij}	A_{ij}	A_{ij}	A_{ji}	a_{ij}	A_{ij}
1	1–2	332.461	-373.942	0.348	0.598	1808.666	245.915	0.318	0.550
	1–3	1229.120	-0.160	0.317	1.970	2248.897	723.989	0.304	1.912
	2–3	2446.890	1302.380	0.167	31.003	1631.324	1402.217	0.258	17.380
2	1–2	391.263	-303.572	0.265	1.260	585.162	1184.298	0.500	3.055
	1–3	1892.510	-460.185	0.282	2.543	1115.590	1147.705	0.485	4.006
	2–3	2067.940	494.310	0.160	30.618	1793.492	468.268	0.155	40.318
3	1–2	1166.300	-291.783	0.202	1.481	1253.989	616.033	0.344	1.481
	1–3	2287.100	-183.950	0.181	1.954	1770.190	846.111	0.339	1.955
	2–3	2349.960	1661.440	0.399	7.870	2212.606	1168.640	0.249	7.874
4	1–2	546.571	-150.197	0.168	2.051	2.051	2.051	2.051	1.481
	1–3	2299.100	-72.187	0.269	2.227	2.227	2.227	2.227	1.955
	2–3	2349.940	611.617	0.158	6.263	6.263	6.263	6.263	7.874
5	1–2	2203.280	152.150	0.319	2.848	1450.995	228.000	0.468	2.848
	1–3	1414.250	-19.610	0.262	2.880	1199.688	171.480	0.410	2.880
	2–3	1156.610	902.890	0.199	26.417	1627.191	1495.390	0.476	26.413
6	1–2	718.490	-350.020	0.156	3.474	822.354	373.761	0.486	3.474
	1–3	1416.000	-253.554	0.448	3.994	1007.923	237.460	0.490	3.994
	2–3	1630.430	570.194	0.274	6.982	2182.877	1171.958	0.392	6.982
7	1–2	1614.230	-317.152	0.202	-3.423	1317.259	348.606	0.393	-3.421
	1–3	913.786	1647.690	0.340	2.320	886.443	822.118	0.393	2.321
	2–3	1999.940	1982.020	0.331	0.707	1996.124	780.712	0.393	0.708
8	1–2	841.486	1596.257	0.353	2.012	1256.108	2131.636	0.290	2.012
	1–3	1452.005	998.742	0.388	2.173	1431.010	1021.001	0.353	2.173
	2–3	1316.861	1018.664	0.317	8.219	2079.796	1749.430	0.452	8.219
9	1–2	741.522	-211.792	0.275	2.111	477.960	2350.571	0.459	2.005
	1–3	1222.370	549.816	0.480	2.851	1398.317	602.968	0.47	3.208
	2–3	1672.420	1349.360	0.297	27.852	2126.787	537.834	0.153	50.000
10	1–2	694.667	-388.136	0.172	3.326	337.318	2191.849	0.478	3.325
	1–3	1105.550	-134.000	0.430	3.469	987.739	2022.673	0.490	3.468
	2–3	2200.000	1145.020	0.359	5.085	1920.268	952.934	0.325	5.084
11	1–2	-204.989	704.990	0.170	2.285	350.795	503.925	0.404	2.285
	1–3	936.160	635.653	0.479	2.839	879.405	853.769	0.436	2.839
	2–3	1748.260	791.847	0.329	3.733	2375.034	978.002	0.335	3.733
12	1–2	-200.378	438.288	0.206	1.854	857.393	623.613	0.392	1.457
	1–3	1741.060	108.973	0.305	2.443	2084.367	916.730	0.348	2.449
	2–3	1737.620	956.303	0.163	23.571	2205.090	917.315	0.176	50
13	1–2	905.115	-272.115	0.171	1.256	1200.128	487.116	0.490	1.226
	1–3	2499.900	533.974	0.328	2.242	1579.257	635.045	0.376	2.300
	2–3	1839.160	1450.190	0.238	36.998	2124.391	1261.642	0.246	50.000
14	1–2	848.574	1072.305	0.455	2.833	665.977	814.838	0.498	2.832
	1–3	1109.720	1479.689	0.429	3.234	2389.324	944.450	0.393	3.234
	2–3	2499.746	1320.741	0.360	8.947	2137.053	1261.558	0.340	8.949
15	1–2	340.847	79.208	0.257	1.580	779.009	610.614	0.468	1.381
	1–3	1493.610	310.828	0.396	2.485	2036.159	805.412	0.372	2.523
	2–3	1989.530	720.570	0.161	37.999	1964.976	663.817	0.152	50.000
16	1–2	674.414	-237.622	0.237	3.003	403.228	1668.606	0.496	3.003
	1–3	1257.920	-235.265	0.393	3.540	1767.738	1507.400	0.476	3.540
	2–3	1632.750	644.722	0.347	5.327	2128.587	655.524	0.293	5.326
17	1–2	736.220	-378.023	0.293	2.718	294.293	1909.581	0.403	2.718
	1–3	1669.349	-361.050	0.306	2.982	2169.359	1729.861	0.413	2.982
	2–3	2143.899	436.847	0.240	5.921	1527.369	175.643	0.166	5.921
18	1–2	2045.840	-190.682	0.174	2.383	1800.158	954.327	0.327	2.383
	1–3	1122.930	873.039	0.370	2.667	1301.322	1178.783	0.359	2.667
	2–3	2101.480	1110.080	0.440	4.883	796.140	522.945	0.480	4.882
19	1–2	719.628	-251.316	0.174	1.428	705.099	325.113	0.418	1.428
	1–3	1422.290	475.905	0.389	2.730	2364.234	801.241	0.336	2.730
	2–3	2234.870	829.965	0.221	24.076	2078.687	572.206	0.172	24.083
20	1–2	-250.213	815.750	0.170	1.880	804.410	744.982	0.425	1.929
	1–3	2308.960	-96.792	0.187	2.295	1976.340	856.057	0.360	2.325
	2–3	1943.820	998.124	0.161	35.104	1931.866	1924.642	0.170	42.644

Table 5. The results of rmsd obtained in this work using MDE, GA and other methods in literature.

Sys. No.	NRTL			Margules	
	Literature	GA	MDE This work	GA	MDE This Work
1	0.0021	0.0013	0.0006	0.0019	0.0018
2	0.0155	0.0038	0.0028	0.0179	0.0139
3	0.0029	0.0008	0.0006	0.0040	0.0040
4	0.0050	0.0008	0.0011	0.0078	0.0078
5	0.0236	0.0039	0.0035	0.0073	0.0073
6	0.0041	0.0024	0.0036	0.0212	0.0212
7	0.0443	0.0031	0.0013	0.0339	0.0339
8	0.0020	0.0004	0.0016	0.0088	0.0087
9	0.0160	0.0059	0.0027	0.0230	0.0227
10	0.0065	0.0030	0.0029	0.0220	0.0219
11	0.0280	0.0062	0.0046	0.0339	0.0338
12	0.0050	0.0018	0.0010	0.0193	0.0184
13	0.0096	0.0038	0.0010	0.0038	0.0032
14	0.0145	0.0048	0.0024	0.0184	0.0184
15	0.0051	0.0027	0.0019	0.0192	0.0187
16	0.0157	0.0036	0.0037	0.0292	0.0291
17	0.0188	0.0060	0.0046	0.0273	0.0272
18	0.0359	0.0051	0.0041	0.0318	0.0317
19	0.0090	0.0028	0.0011	0.0130	0.0130
20	0.0108	0.0056	0.0009	0.0035	0.0033
Overall	0.0159	0.0039	0.0023	0.0195	0.0170

Table 6. Results obtained for RND problem using DE and MDE.

Algorithm	**FES**	**Best**	**Worst**	**Mean**	**Median**	**Std-Dev**
DE	10000	0.388811	0.388453	0.388789	0.388793	1.81E-05
	15000	0.388811	0.388804	0.388811	0.388811	2.46E-07
	20000	0.388811	0.388811	0.388811	0.388811	2.88E-09
	50000	0.388811	0.388811	0.388811	0.388811	0
	100000	0.388811	0.388811	0.388811	0.388811	0
MDE	10000	0.388811	0.388723	0.388807	0.388806	4.62E-06
	15000	0.388811	0.3811	0.388811	0.388811	2.92E-08
	20000	0.388811	0.388811	0.388811	0.388811	2E-10
	50000	0.388811	0.388811	0.388811	0.388811	0
	100000	0.388811	0.388811	0.388811	0.388811	0

Table 7. Number of function evaluations (FES), CPU time and function value

Problem		**DE**	**MDE**
RND	No. of function Evaluations	14283	12699
	CPU Time (s)	3.634823	2.979619
	Function Value (Cost)	0.388811	0.388811

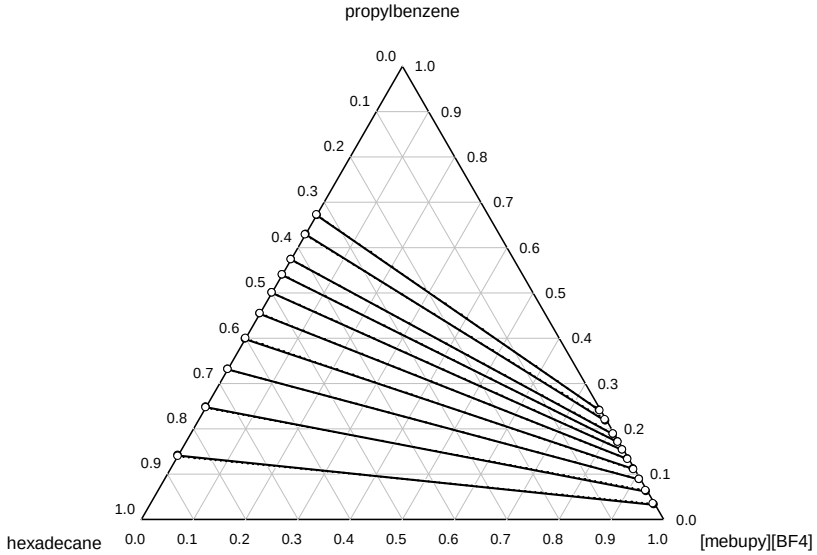

Figure 4. Tie-lines for system no. 1, NRTL model, solid lines and full points: predicted tie-lines with GA; dashed lines and empty points: predicted tie-lines with MDE.

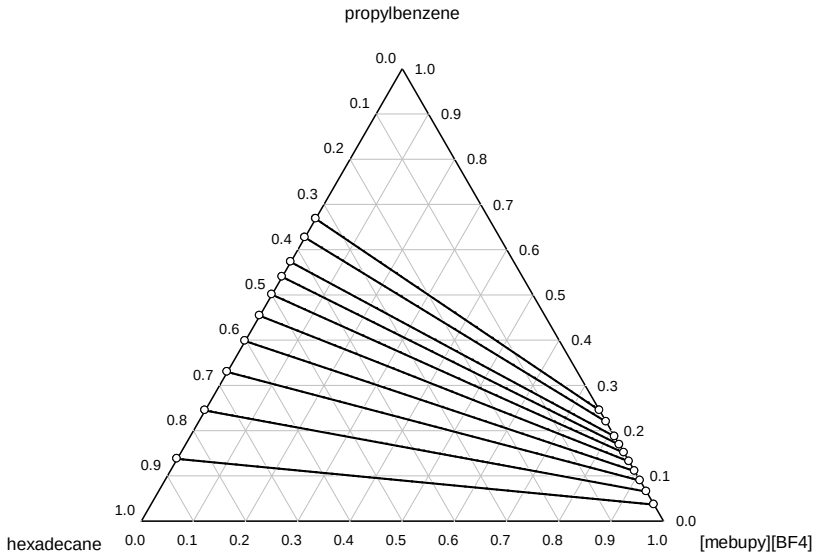

Figure 5. Tie-lines for system no. 1, Two-Suffix Margules model, solid lines and full points: predicted tie-lines with GA; dashed lines and empty points: predicted tie-lines with MDE.

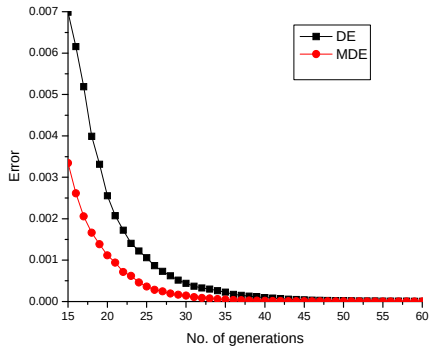

Figure 6. Error against number of generations for reactor network design problem.

model outperformed the Two-Suffix Margules model by predicting more accurate (with one order of magnitude) rmsd values. The results obtained in this work using MDE are better compared to the results obtained using GA and other traditional algorithms. This study can be extended for the calculation of some other activity coefficient models using similar approach. For RND problem MDE algorithm outperforms DE in terms of number of function evaluations.

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References

Alkhaldi KHAE, Al-Tuwaim MS, Fandary MS, Al-Jimaz AS (2011), Separation of propylbenzene and n-alkanes from their mixtures using 4-methyl-N-butylpyridinium tetrafluoroborate as an ionic solvent at several temperatures. Fluid Phase Equilibria 309: 102–107.

Al-Maamari RS, Vakili-Nezhaad G, Vatani M (2015), Experimental and modeling investigations of the viscosity of crude oil binary blends: New Models Based on the Genetic Algorithm Method. *The Journal of Engineering Research* 11: 81-91.

Angira R (2006), Evolutionary Computation for Optimization of Selected Non-linear Chemical Processes. Ph.D. Thesis (BITS-Pilani, India).

Angira R, Babu BV (2006), Optimization of process synthesis and design problems: A modified differential evolution approach. *Chemical Engineering Science* 61: 4707-4721.

Babu BV, Angira R (2006), Modified differential evolution (MDE) for optimization of non-linear chemical processes. *Computers and Chemical Engineering* 30: 989-1002.

Colaco MJ, Dulikravich GS, Martin TJ (2004), optimization of wall electrodes for electro-hydrodynamic control of natural convection during solidification. *Materials and Manufacturing Processes* 19: 719–736.

Dománska U, Pobudkowska A, Krolikowski M (2007), Separation of aromatic hydrocarbons from alkanes using ammonium ionic liquid C2NTf2 at T = 298.15 K. *Fluid Phase Equilibria* 259: 173–179.

Domínguez I, González EJ, González R, Domínguez A (2011), Extraction of benzene from aliphatic compounds using commercial ionic liquids as solvents: study of the liquid–liquid equilibrium at t = 298.15 K. *Journal of Chemical and Engineering Data* 56: 3376–3383.

Fan HY, Lampinen J (2003), Trigonometric mutation operation to differential evolution. *Journal of Global Optimization* 27: 105–129.

García J, Fernández A, Torrecilla J, Oliet M, Rodríguez F (2009), Liquid–liquid equilibria for {hexane + benzene + 1-ethyl-3-methylimidazolium ethylsulfate} at (298.2, 313.2 and 328.2) K. Fluid Phase Equilibria 282: 117–120.

García J, Fernández A, Torrecilla J, Oliet M, Rodríguez F (2010a), Ternary liquid−liquid equilibria measurement for hexane and benzene with the ionic liquid 1-Butyl-3-methylimidazolium methylsulfate at T = (298.2, 313.2, and 328.2) K. *Journal of Chemical and Engineering Data* 55: 258–261.

García J, García S, Torrecilla J, Oliet M, Rodríguez F (2010b), Liquid−liquid equilibria for the ternary systems {Heptane + Toluene + N-Butylpyridinium Tetrafluoroborate or N-Hexylpyridinium Tetrafluoroborate} at T = 313.2 K. *Journal of Chemical and Engineering Data* 55: 2862–2865.

Gujarathi AM, Babu BV (2009a), Improved multi objective differential evolution (MODE) approach for purified terephthalic acid (PTA) Oxidation Process. *Materials and Manufacturing Processes* 24: 303-319.

Gujarathi AM, Babu BV (2009b), Optimization of adiabatic styrene reactor: A hybrid multi objective differential evolution (H-MODE) Approach. *Industrial and Engineering Chemistry Research* 48: 11115–11132.

Gujarathi AM, Babu BV (2010a), Advances in optimization and simulation of low density polyethylene (LDPE) tubular reactor. *In Handbook of Research on Chemo informatics and Chemical Engineering*, Edited by A K Haghi, Nova Science Publishers, USA 109-138.

Gujarathi AM, Babu BV (2010b), Multi-objective optimization of industrial styrene reactor: Adiabatic and pseudo-isothermal operation. *Chemical Engineering Science* 65: 2009-2026.

Gujarathi AM, Babu BV (2011), Multiobjective optimization of industrial processes using elitist multi objective differential evolution (Elitist-MODE). *Materials and Manufacturing Processes* 26: 455-463.

Gutierrez JP, Meindersma W, de Haan AB (2011), Binary and ternary (liquid + liquid) equilibrium for {methylcyclohexane (1) + toluene (2) + 1-hexyl-3-methylimidazolium tetracyanoborate (3)/1-butyl-3-methylimidazolium tetracyanoborate (3). *The*

Journal of Chemical Thermodynamics 43: 1672–1677.

Hansmeier AR, Jongmans M, Meindersma GW, de Haan AB (2010a), LLE data for the ionic liquid 3-methyl-N-butyl pyridinium dicyanamide with several aromatic and aliphatic hydrocarbons. *The Journal of Chemical Thermodynamics* 42: 484–490.

Hansmeier AR, Minoves Ruiz M, Meindersma GW, de Haan AB (2010b), Liquid−liquid equilibria for the three ternary systems (3-methyl-N-butylpyridinium dicyanamide + Toluene + Heptane), (1-Butyl-3-methylimidazolium Dicyanamide + Toluene + Heptane) and (1-Butyl-3-methylimidazolium Thiocyanate + Toluene + Heptane) at T = (313.15 and 348.15) K and p = 0.1 MPa. *Journal of Chemical and Engineering Data* 55: 708–713.

Holland JH (1992), Algoritmos geneticos. *Investigacion Y Ciencia* 192: 38–45.

Kirkpatrick S, Gelatt CD, Vecchi MP (1983), Optimization by simulated annealing. *Science* 220: 671–680.

Lei Z, Zhang J, Li Q, Chen B (2009), UNIFAC model for ionic liquids. *Industrial and Engineering Chemistry Research* 48: 2697-2704.

Letcher TM, Deenadayalu N (2003), Ternary liquid–liquid equilibria for mixtures of 1-methyl- 3 – octyl - imidazolium chlorideþbenzeneþan alkane at T=298.2K and 1 atm. *The Journal of Chemical Thermodynamics* 35: 67–76.

Letcher TM, Reddy P (2005), Ternary (liquid+liquid) equilibria for mixtures of 1-hexyl-3-methylimidazolium (tetrafluoroborate or hexafluorophosphate)+benzene+alkane at T=298.2 K and p=0.1 MPa. *The Journal of Chemical Thermodynamics* 37: 415–421.

Maduro RM, Aznar M (2008), Liquid–liquid equilibrium of ternary systems 1-butyl-3-methylimidazolium hexafluorophosphate + aromatic + aliphatic. *Fluid Phase Equilibria* 265: 129–138.

Maduro RM, Aznar M (2010), Liquid–liquid equilibrium of ternary systems 1-octyl-3-methylimidazolium hexafluorophosphate + aromatic + aliphatic hydrocarbons. *Fluid Phase Equilibria* 296: 88–94.

Pereiro AB, Rodriguez A (2009), Application of the ionic liquid Ammoeng 102 for aromatic/aliphatic hydrocarbon separation. *The Journal of Chemical Thermodynamics* 41: 951–956.

Prausnitz JM, Lichtenthaler RN, Azevedo EG (1999), Molecular thermodynamics of fluid phase equilibria, third ed., Prentice-Hall, New York.

Price KV, Storn RM, Lampinen JA (2005), Differential evolution: A practical approach to global optimization. Springer, Berlin Heidelberg.

Rashtchian D, Ovaysi S, Taghikhani V, Ghotbi C (2007), Application of the genetic algorithm to calculate the interaction parameters for multiphase and multicomponent systems. *Iranian Journal of Chemistry and Chemical Engineering* 26: 89-102.

Renon H, Prausnitz J M (1968), Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE Journal* 14: 135–144.

Revelli AL, Mutelet F, Jaubert JN (2010), Extraction of benzene or thiophene from n-heptane using ionic liquids. NMR and thermodynamic study. *The Journal of Physical Chemistry* B 114: 4600-4608.

Ryoo HS, Sahinidis NV (1995), Global optimization of nonconvex NLPs and MINLPs with applications in process design. *Computers and Chemical Engineering* 19: 551–566.

Sahoo RK, Banerjee T, Ahmad SA, Khanna A (2006), Improved binary parameters using GA for multi-component aromatic extraction: NRTL model without and with closure equations. *Fluid Phase Equilibria* 239: 107–119.

Sahoo RK, Banerjee T, Khanna A (2007), UNIQUAC interaction parameters with closure for imidazolium based ionic liquid systems using genetic algorithm. *The Canadian Journal of Chemical Engineering* 85: 833–853.

Seader JD, Henley E J (2006), Separation process principles, second ed., John Wiley and Sons, Inc., New York.

Selvan MS, McKinley MD, Dubois RH, Atwood JL (2000), Liquid−liquid equilibria for toluene + heptane + 1-Ethyl-3-methylimidazolium triiodide and toluene + heptane + 1-Butyl-3-methylimidazolium triiodide. *Journal of Chemical and Engineering Data* 45: 841-845.

Singh MK, Banerjee T, Khanna A (2005), Genetic algorithm to estimate interaction parameters of multicomponent systems for liquid–liquid equilibria. *Computers and Chemical Engineering* 29: 1712–1719.

Stragevitch L, Davila SG (1997), Application of a generalized maximum likelihood method in the reduction of multicomponent liquid-liquid equilibrium data. *Brazilian Journal of Chemical Engineering* 14: 41–52.

Stumberger G, Dolinar D, Pahner U, Hameyer K (2000), Optimization of radial active magnetic bearings using the finite element technique and the differential evolution algorithm. *IEEE Transactions on Magnetics* 36: 1009–1013.

Vakili-Nezhaad G, Vatani M, Asghari M (2013), Calculation of the binary interaction and nonrandomness parameters of NRTL, NRTL1, and NRTL2 models using genetic algorithm for ternary ionic liquid systems. *Chemical Engineering Communications* 200: 1102–1120.

Vakili-Nezhaad G, Vatani M, Gujarathi AM (2014), Application of genetic algorithm to calculation of three-suffix margules parameters in ternary extraction ionic liquid systems. *International Journal of Thermodynamics* 17: 1-6.

Vatani M, Asghari M, Vakili-Nezhaad G (2012), Application of genetic algorithm to the calculation of parameters for NRTL and twosuffix margules models in ternary extraction ionic liquid systems. *Journal of Industrial and Engineering Chemistry* 18: 1715–1720.

Zhou T, Wang Z, Chen L, Ye Y, Qi Z, Freund H, Sundmacher K (2012), Evaluation of the ionic liquids 1-alkyl-3-methylimidazolium hexafluorophosphate as a solvent for the extraction of benzene from cyclohexane: (Liquid + liquid) equilibria. *The Journal of Chemical Thermodynamics* 48: 145–149.