Optimization of Extended UNIQUAC Parameter for Activity Coefficients of Ions of an Electrolyte System using Genetic Algorithms


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(Received 13 January 2017; Received in revised form 29 May 2017; accepted 7 June 2017)

Abstract – In the present research, in order to predict activity coefficient of inorganic ions in electrolyte solution of a petroleum system, we studied 13 components in the electrolyte solution, including H₂O, CO₂ (aq), H⁺, Na⁺, Ba²⁺, Ca²⁺, Sr²⁺, Mg²⁺, SO₄, CO₃, OH⁻, Cl⁻, and HCO₃⁻. To predict the activity coefficient of the components of the petroleum system (a solid/liquid equilibrium system), activity coefficient model of Extended UNIQUAC was studied, along with its adjustable parameters optimized based on a genetic algorithm. The total calculated error associated with optimizing the adjustable parameters of Extended UNIQUAC model considering the 13 components under study at three temperature levels (298.15, 323.15, and 373.15 K) using the genetic algorithm is found to be 0.07.

Key words: Mineral ions, Optimization, Genetic Algorithms, Extended UNIQUAC Model

1. Introduction

Optimization is the process of maximizing the desirable efficiency. Optimization techniques implement this process by undertaking some modifications on an initial assumption. To increase the efficiency, optimization algorithms should apply operators on initial points to produce new points within the search space for objective function (to gradually move toward the optimal locations within this space). In most of these search techniques (gradient method), the algorithm proceeds from one point to another; in most cases, this point-by-point approach ends up with optimization errors as they converge to a local maxima. This drawback in optimization of nonlinear models leads to complex issues in the process of problem solving. To overcome this drawback [1-3] powerful algorithms such as genetic algorithms (GA) are proposed. Electrolyte solutions are listed among the most important aqueous systems in chemical industries, such as petroleum systems, due to the electrostatic and short-range forces established between ions and solvent. Either high or low concentration can lead to a non-ideal behavior in the electrolyte systems. In this regards it is necessary to investigate all inter-particle forces. Due to the dependence of saturation index of mineral sediment formation based on the nature and activity of mineral ions in water systems of industrial operations such as oil, in this research in order to predict activity factor of mineral ions in oil systems, 13 components of electrolytic solutions have been studied: H₂O, CO₂ (aq, H⁺, Na⁺, Ba²⁺, Ca²⁺, Sr²⁺, Mg²⁺, SO₄, CO₃, OH⁻, Cl⁻ and HCO₃⁻). Considering the satisfying efficiency of the activity coefficient model of Extended UNIQUAC with its adjustable parameters optimized using genetic algorithms, we used this method to investigate the activity coefficient of the ions in this study.

2. Theoretical Section

2-1. Extended UNIQUAC Model

Thomsen and Rasmussen (1999)[4] exercised Extended UNIQUAC model to study the electrolytic systems. Satisfying results were
acquired for the solid-liquid, liquid-liquid and vapor-liquid equilibrium systems. The model is a combination of local composition model (UNIQUAC) and Debye-Hückel term. UNIQUAC model was suggested by Abrams and Prausnitz [5] to describe the Gibb’s additional energy of the mixture, and includes two parts: one part of the compound is related to the entropy of the system and is determined according to the size and shape of molecule, the remaining part considers the intermolecular forces involved in mixing enthalpy and depends on molecular forces.

UNIQUAC equation has adjustable parameters and is expressed as follows for the equilibrium of liquid-solid systems (multi-part) [4-6]:

$$G^E = G^E_{\text{combinatorial}} + G^E_{\text{Residual}} + G^E_{\text{Debye-Hückel}}$$ \hspace{1cm} (1)

$$\frac{G_{\text{Residual}}^E}{RT} = \sum x_i n_i \ln \left( \frac{Z^i}{x_i} \right) \frac{Z}{2} \sum q_i x_i \ln \left( \frac{\theta_i}{\phi_i} \right)$$ \hspace{1cm} (2)

In the upper equation, $G^E$ is Gibbs free energy, $z$ is coordination number with a value of 10; $x_i$ is mole fraction; $\phi_i$ is mole fraction; $q_i$ is volume fraction and $\theta_i$ is the surface area fraction of ions in the liquid-solid or liquid-vapor equilibrium system which is expressed as:

$$\phi_i = \frac{x_i r_i}{\sum x_i r_i}$$ \hspace{1cm} (3)

$$\theta_i = \frac{x_i q_i}{\sum x_i q_i}$$ \hspace{1cm} (4)

where $r_i$ and $q_i$ are the volume and surface area parameters for each ion. Also, for the residual term, the following equation holds:

$$\frac{G_{\text{Residual}}^E}{RT} = -\sum x_i n_i \ln (\sum \phi_i)$$ \hspace{1cm} (5)

$$\varphi_{ij} = \exp \left( \frac{u_{ij} - u_{ii}}{RT} \right)$$ \hspace{1cm} (6)

where $u_{ij}$ is the interaction energy between similar ions in an equilibrium system of solid-liquid and vapor-liquid. $u_{ij}$ is the interaction energy between different ions in an equilibrium system. The interaction energy is a function of temperature and is defined as:

$$u_{ij} = u_{ij}^0 + u_{ij}^\prime (T - 298.15)$$ \hspace{1cm} (7)

where $u_{ij}^0$ and $u_{ij}^\prime$ are two adjustable parameters for interaction energy between the ions in the equilibrium system.

The Debye-Hückel contribution (to the Gibb's excess energy) of the extended UNIQUAC model is given by the expression:

$$\frac{G_{\text{Debye-Hückel}}^E}{RT} = -x_i m_i \frac{4A}{b_i^3} \left[ \ln \left( 1 + b_i^{1/2} \right) - b_i^{1/2} + b_i^{1/2} \right]$$ \hspace{1cm} (8)

where $M_i$ is the molar mass of water, $x_i$ is the mole fraction of water, $A$ is a Debye-Hückel parameter, $b$ is a constant value equal to $1.5 \left( \frac{\text{m}^2}{\text{mol}} \right) F^2$, and $l$ is the ionic strength.

$$I = 0.5 \sum m_i Z_i^2$$ \hspace{1cm} (9)

In Eq. 9, $z_i$ is the charge and $m_i$ is the molality (mol (kg H_2O)^-1) of ion i. Considering the relationship between excess Gibbs free energy and basic equations of thermodynamics, by differentiation of Equation 1 against with respect to the mole fraction of different species, the activity coefficient for each ion is derived:

$$\ln \gamma_i = \frac{\gamma_i^E - \gamma_i^E_0}{\gamma_i^E_0}$$ \hspace{1cm} (10)

$$\ln \gamma_i = \ln \left( \gamma_i^\text{Residual} \right) + \ln \left( \gamma_i^\text{combinatorial} \right) + \ln \left( \gamma_i^\text{Debye-Hückel} \right)$$ \hspace{1cm} (11)

To normalize Equation 11 for electrolyte system, considering water existence (as a solvent) and its ions of solute, we have:

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 0$$ \hspace{1cm} (12)

$$\gamma_i^* = \frac{\gamma_i}{\gamma_i^0}$$ \hspace{1cm} (13)

In Eq. 13, for $\gamma_i^*$ (activity coefficient of ion at infinite dilution), we have:

$$\gamma_i^* = \lim_{x_i \rightarrow 0} \gamma_i$$ \hspace{1cm} (14)

And finally, we have:

$$\ln \gamma_i^* = \ln \left( \frac{\gamma_i}{\gamma_i^0} \right) + z_i \ln \left( \frac{\gamma_i}{\gamma_i^0} \right) + q_i \ln \left( \frac{\gamma_i}{\gamma_i^0} \right) + q_i \ln \left( \frac{\gamma_i}{\gamma_i^0} \right) + q_i \ln \left( \frac{\gamma_i}{\gamma_i^0} \right) - \sum \theta_i \ln \left( \frac{\gamma_i}{\gamma_i^0} \right)$$

$$-q_i \left[ 1 - \ln \left( \frac{\phi_i}{\phi_i^0} \right) \right] - Z_i \frac{A_1^{1/2}}{1 + b_i^{1/2}}$$ \hspace{1cm} (15)

2-2. Genetic Algorithms

First introduced by John Holland, the genetic algorithm is indeed a special case of evolutionary algorithm. It only requires some information about the quality of generated solutions using each set of variables, whereas some other optimization techniques require detailed information and recognition of the problem structure and variables [7,8].

As a numerical optimization technique, genetic algorithms considers a set of points within the solution space and searches different points across this space at each iteration. This algorithm works without any limitation regarding the function to be optimized (e.g., differentiability) and, in the process of searching for a solution, it only requires the evaluation of the objective function at different points. According to these features genetic algorithms can be considered as a reliable technique in case of different linear and non-linear problems. In each iteration, each string in the set of available strings will be decoded and its value is evaluated using the objective function. Based on the evaluated values, a fitness value is assigned to each string. This fitness value determines the probability for each string to be selected among the population of the strings. Accordingly to the selection probabilities, a set of strings is selected. By applying genetic operators on the selected strings, new strings are selected to replace some of the strings from the initial population; this is done to keep
the number of strings constant at different iterations. In genetic algorithms, not only genetic operators search for new points in the solution space at each iteration, but also the selection process searches the regions within the solution space where the statistical average of the objective function considered by the user is higher in value [8,9]. In genetic algorithms, using strings of either constant or variable lengths, a set of design variables is coded, with each string representing a solution point in computational search space.

These algorithms begin with producing a generation where a so-called “initial population” is generated either selectively or randomly. The existing population is selected according to the fitness of each individual in the population for the next generation. Thereafter, genetic operators, such as selection, crossover or mutation, are applied and finally a new population is established. Consequently, new generations replace older ones and the cycles continue until a solution is reached [8-10]. Then genetic algorithm does not require detailed information about the problems under study. Considering that its decisions are principally made randomly, all possible solutions are achievable theoretically. Among other strengths of genetic algorithm, one can refer to the following [8-11]:

1. It does not need to calculate derivatives of functions.
2. It can undertake the optimization process using either continuous or discrete variables.
3. It can undertake the optimization process using a large number of variables.
4. It is capable of obtaining several solutions at the same time.
5. It is applicable on sets of solutions.

Many researchers have made use of genetic algorithms to solve complex linear or non-linear engineering and chemical problems and issues, including Agrawal et al. [12] (in optimizing low-density polyethylene reactor), Cao et al. [13] (in optimizing the minimum consumption of fresh water), Elliot et al. [14] (in optimizing aviation fuel combustion), Jezowski et al. [15] (in optimizing retrofitting thermal transducer) and Masoori et al. [16] (in optimizing reaction rate in reactive systems), and the results demonstrate the efficiency of using genetic algorithms in optimization and objective function problems. System problems and industrial and chemical process optimization are among the other usages of genetic algorithms as stated by Till et al. [17], Young et al. [18] and Lepar et al. [19].

Fig. 1 provides a flowchart of optimization and calculation of activity coefficient of ions in a petroleum system (under solid/liquid equilibrium) using genetic algorithm. According to this flowchart, we begin with calling three constant terms, R, temperature variations, and initial concentration in molality. Since the activity coefficient model of Extended UNIQUAC is calculated based on molar ratios, the initial concentration should be unit-converted from molality to molar ratio. In Extended UNIQUAC model, three important parameters comprise the main axis of the model: \( u \) with all of them being optimizable and adjustable. However, the parameter \( u \) is more important than the others due to its dependence on temperature con-

<table>
<thead>
<tr>
<th>Components of Electrolytic system</th>
<th>Initial concentration (molality)</th>
<th>Activity Coefficient at 298.15 k</th>
<th>Activity Coefficient at 323.15 k</th>
<th>Activity Coefficient at 373.15 k</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>55.5</td>
<td>0.8506</td>
<td>0.8507</td>
<td>0.8554</td>
</tr>
<tr>
<td>CO(_2)(aq)</td>
<td>0.00867</td>
<td>1.8095</td>
<td>1.8091</td>
<td>1.8088</td>
</tr>
<tr>
<td>H(^+)</td>
<td>0.00401</td>
<td>1.9810</td>
<td>1.3059</td>
<td>0.9719</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>3.14</td>
<td>0.7263</td>
<td>0.7373</td>
<td>0.6649</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>0.000112</td>
<td>0.1510</td>
<td>0.1326</td>
<td>0.0793</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>0.311</td>
<td>0.4019</td>
<td>0.3199</td>
<td>0.1876</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>0.0172</td>
<td>0.3578</td>
<td>0.2679</td>
<td>0.1312</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.0981</td>
<td>0.6378</td>
<td>0.4617</td>
<td>0.2359</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>2.96E-12</td>
<td>0.3631</td>
<td>0.3471</td>
<td>0.2818</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>4.05</td>
<td>0.9317</td>
<td>0.9327</td>
<td>0.8462</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>0.00406</td>
<td>0.0233</td>
<td>0.0272</td>
<td>0.0227</td>
</tr>
<tr>
<td>CO(_3^{2-})</td>
<td>2.92E-13</td>
<td>0.0160</td>
<td>0.0138</td>
<td>0.0052</td>
</tr>
<tr>
<td>HCO(_3)</td>
<td>0.0113</td>
<td>0.7098</td>
<td>0.7218</td>
<td>0.5851</td>
</tr>
</tbody>
</table>
ditions. The three parameters were used in the optimization algorithm and then, the activity coefficient was calculated in molar ratio, and once unit-converted to molality, it was fed into a trial and error loop. The optimization process stops as soon the error satisfies the predefined error criterion and the results are printed. The computation process continues until the error criterion is met.

3. Data Used in this Study

In this research, in order to investigate activity coefficient of ions in a petroleum system, the activity coefficient model of Extended UNIQUAC was studied. The adjustable parameters of this model were optimized according to the equilibrium concentration and activity coefficient (according to Pars Scale Simulator of The Research Institute of Petroleum Industry of Iran) presented in Table 1.

4. Results and Discussion

4-1. Results of parameter optimization of the model

The process denoted in the flowchart in Fig. 1 was performed on the data. After running the application for the equilibrium concentrations presented in Table 1 and temperature variations of 298.15, 323.15, and 373.15 K, the error equation \( \sum_{i,j} q_i \sigma_{ij} \) represents a total calculated error equal to 0.07. Fig. 2 shows the trend of GA iterations as the optimization process continued to reach a desirable total error (at three temperature levels of 298.15, 323.15, and 373.15 K). Table 2 represents optimal values of the parameters \( r \) and \( q \). Tables 3 and 4 represent the values of \( u_o \) and \( u_t \), respectively.

In Figs. 3–5, the trend of the GA iteration is represented for the 13 components in the electrolyte solution including water, dissolved carbon dioxide, hydrogen, sodium, barium, calcium, strontium, magnesium hydroxide, chloride, sulfate, carbonate and bicarbonate at three different temperatures (298.15, 323.15, and 373.15 K).

Table 2. Optimization of parameters \( r \) and \( q \) for UNIQUAC equation fitted to experimental data [6,20]

<table>
<thead>
<tr>
<th>Electrolyte solution components</th>
<th>( r )</th>
<th>( q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>0.92</td>
<td>1.4</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.75</td>
<td>2.45</td>
</tr>
<tr>
<td>H</td>
<td>0.14</td>
<td>0.1E-15</td>
</tr>
<tr>
<td>Na</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Ba</td>
<td>15.67</td>
<td>14.48</td>
</tr>
<tr>
<td>Ca</td>
<td>3.87</td>
<td>1.48</td>
</tr>
<tr>
<td>Sr</td>
<td>7.14</td>
<td>12.89</td>
</tr>
<tr>
<td>Mg</td>
<td>5.41</td>
<td>2.54</td>
</tr>
<tr>
<td>OH</td>
<td>9.4</td>
<td>8.88</td>
</tr>
<tr>
<td>Cl</td>
<td>10.39</td>
<td>10.2</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>12.79</td>
<td>12.44</td>
</tr>
<tr>
<td>CO(_3)</td>
<td>10.83</td>
<td>10.77</td>
</tr>
<tr>
<td>HCO(_3)</td>
<td>8.08</td>
<td>8.68</td>
</tr>
</tbody>
</table>

1Pars Scale Simulator
4-2. Comparing the results of genetic algorithms with other algorithms

Fig. 6 provides a comparison between the optimization of Extended UNIQUAC model based on three algorithms: Imperialist Competitive Algorithm (ICA) [21], Particle Swarm Optimization Algorithm (PSO) [22-23] and Artificial Bee Colony Algorithm (ABC) [24-26]. Based on the flowchart in Fig. 1, the associated error with the optimization of the parameters of the considered model in this research using IC, PSO and ABC algorithms was found to be 0.054, 0.1045, and 0.089, respectively. Whereas, the associated error with the application of the proposed GA in the present research was 0.07, emphasizing superior quality and accuracy of the genetic algorithms compared to the aforementioned algorithms.

4-3. Comparing the optimized theoretical model with experimental results

Fig. 7 compares solubility predictions of three electrolyte systems using IC, PSSO and ABC algorithms with other algorithms.

Table 4. \( \nu_{ij} = u_{ji} \) parameter of energy interaction between ions for aqueous electrolyte systems in UNIQUAC equation

| Solution components | \( \text{H}_2\text{O} \) | \( \text{CO}_2 \) | H | Na | Ca | Ba | Sr | mg | OH | Cl | S| SO4 | CO3 | HCO3 |
|---------------------|----------------|-------------|---|----|----|----|----|----|----|----|    |   |    |    |     |
| \( \text{CO}_2\text{aq} \) | 2.01 | 0.002 | | | | | | | | | | | | | |
| H | -5.66 | -2.06 | 0.0012 | | | | | | | | | | | | |
| Na | 1.9 | -2.83 | 5.001 | 0.00203 | | | | | | | | | | | |
| Ca | 5.81 | -6.03 | 4.28 | -0.062 | 0.032 | | | | | | | | | | |
| Ba | 24.75 | -6.2523 | -5.624 | 1.47 | 2.63 | 0.0001 | | | | | | | | | |
| Sr | 8.4 | 1.9344 | 4.34 | -4.5 | -2.88 | 6.97 | 0.0011 | | | | | | | | |
| Mg | 7.97 | -7.11 | -2.23 | 5.7 | 4.73 | 12.4 | 5.62 | 0.0025 | | | | | | | |
| OH | -1.97 | 4.75 | -4.02 | -3.27 | 3.95 | 5.96 | 1.35 | 7.9 | 1.54 | | | | | |
| Cl | -2.95 | -2.04 | -5.411 | -1.46 | 9.16 | 0.93 | -5.4 | 6.77 | -5.2 | 7.3 | | | | |
| SO4 | -2.64 | 1.34 | -5.2 | -2.463 | -1.069 | -0.54 | 1.25 | 2.44 | 14.98 | 2.44 | 6.7 | | | |
| CO3 | -6.54 | -6.25 | 0.004 | 2.5113 | 7.64 | 6.59 | -4.5 | 0.03 | -0.4 | 7.7 | -6.56 | -0.46 | | |
| HCO3 | 2 | 3.1 | -2.3 | 1.3 | -1.9 | 2.5 | 3.1 | 1.91 | 1 | 1.23 | 2.6 | 2.3 | 2.9 | | |

Fig. 3. Optimization of activity coefficient of components of electrolyte solution using genetic algorithms (GA) at 298.15 K.

Fig. 4. Optimization of activity coefficient of components of electrolyte solution using genetic algorithms (GA) at 323.15 K.
at the constant pressure of 1 bar and two different temperatures of 323 and 368 K using the theoretically optimized model in this research to experimental results. According to the results of Fig. 7, solubility of barium sulfate at 323 K increases as does the concentration of sodium chloride. This is also true for the solubility of strontium sulfate in presence of magnesium chloride and calcium chloride at 368 K, as the increase in the concentration of magnesium chloride and calcium chloride leads to an increase in the concentration of strontium sulfate. Comparing the results demonstrated in Fig. 7 emphasizes that the optimized model in this research is significantly acceptable.

5. Conclusion

Considering the efficiency of the activity coefficient model of Extended UNIQUAC with optimized parameters was studied to predict activity coefficient of inorganic ions in petroleum systems (under solid-liquid equilibrium). The parameters of Extended UNIQUAC model were optimized by using genetic optimization algorithm. To apply trial and error on the results, the Pscalsim Software released by Research Institute of Petroleum Industry (RIPI) was used as the comparison reference. The total error calculated for the 13 ions under three temperatures of 298.15, 323.15, and 373.15 K using the genetic algorithm was found to be 0.07, and the iteration trend of the algorithm was reported for the 13 components of the system under study at three temperatures of 298.15, 323.15, and 373.15 K. The results obtained using the genetic algorithm demonstrate the importance and priority of exploiting the optimized Extended UNIQUAC model in case of investigating saturation index of inorganic precipitates.
Fig. 7. Comparison between solubility values (molar) predicted by Extended UNIQUAC model and experimental data: a) BaSO₄-NaCl-H₂O (at pressure: 1 bar and Temperatures: 323.15 K & Experimental reference [27]). b) SrSO₄-MgCl₂-H₂O (at pressure: 1 bar and Temperatures: 368.15 K & Experimental reference [28]). c) SrSO₄-CaCl₂-H₂O (at pressure: 1 bar and Temperatures: 368.15 K & Experimental reference [28]).

References


(2007).