



Prediction of Water Activity of Electrolyte Solutions with Extended UNIQUAC Model

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ABSTRACT

In the present study, in order to predict the Water activity of aqueous electrolyte system, 21 cases have been regarded aqueous solution ($ACLx=1,2; A=Li,H,Na,K,NH_4,Cs,Mg,Ca,Ba$ and $Bj=1,2SO_4; B=Li,Na,K,NH_4,Mg,Mn,Ni,Cu,Zn$ and $NaCl+LaCl_3(aq)$, $NaCl+MgCl(aq)$, $Na_2SO_4+MgSO_4(aq)$). For this study, Extended UNIQUAC Thermodynamic model is desired, that adjustable parameters, are optimized with genetic algorithm. Results Extended UNIQUAC model optimization by genetic algorithms, has produced favorable results; so that the minimum and maximum total system error electrolyte is 0.00017 and 0.05, respectively. For electrolyte system, in this study, temperature 298.15, and the pressure of 1 bar is considered. The maximum concentration of 6 has been studied.

Keywords: Mineral ions; Genetic algorithm; Extended UNIQUAC model; Electrolyte solutions

INTRODUCTION

The thermodynamic properties of aqueous electrolyte solutions are required for industrial processes. Electrolyte material that in soluble, ionic form and is strictly non-ideal (due to long-range forces). So to review these materials, according to the activity coefficient of ions and solvents (such as water), in dilute and concentrated solutions is essential. In recent decades, the study of water activity in aqueous systems has been more attention. Choudhury and Le Maguer[1], by using UNIFAC Model, water activity studied in glucose solution and Ha and Chen [2] used Zdanovskii-Stokes- Robinson (ZSR) and the Kusik and Meissner (KM) equations to predict water activity in aqueous systems containing $MgCl_2$, $Mg(NO_3)_2$ and $MgSO_4$. Wang at al [3], describe Pitzer Model to estimate water activity in aqueous systems containing $MSO_4(M=Ni,Cu, Zn, Mn, Co)$. Kawaguchi et al[4-5] and Correa [6] used ASOG group contribution method to predict the water activity of aqueous electrolyte solutions. However, experimental studies, water activity measurements were carried out in the field, that studies ,Apelblat and Korin (1998)[7] ,Hubert at el [8] ,Robinson and Macaskill [9], Taylor [10], Moore at el [11], Hellams at el [12] , Soldano and Patterson [13] is remarkable. Electrolyte solutions, due to electrostatic forces between the ions and short-range forces between the ions and solvents, of the most important types of water systems in the chemical industry (such as petroleum system) is. So that at low concentrations and high intensity makes non-ideal behavior electrolyte system. Therefore, it is necessary to review all the forces between particles. For this study, optimize the parameters ENIQUAC model to determine the effect of temperature in order to change the water activities electrolyte system to comprehensively investigated. Results EUNIQUAC model, the importance of optimized model (in this study) to study water activities, in order to prediction of mineral deposits index has doubled, that following equation, the emphasis on this issue:

$$K_{sp} = M_{\pm} \gamma_{\pm} a_w^n$$

Due to the importance of water activity, to predict the saturation index of mineral deposits, in the electrolytic system and also the lack of a comprehensive study of electrolyte in previous studies, in this study, water activity according to Extended UNIQUAC model and genetic algorithm is studied.

The model and solution method

The extended UNIQUAC activity coefficient equation:

In this work, model Extended UNIQUAC (as presented by Thomsen and Rasmussen (1999)[14]) is desired to study the electrolytic system. This model is a combination of UNIQUAC model and Debye-Hückel term. UNIQUAC equation presented by Abrams and Prausnitz[15] for excess Gibbs free energy of a mixture and consists of two parts: first part is combinatorial that is related to the entropy of the system and has been determined based on the size and shape of the molecules. The residual part is related to intermolecular forces involved in the enthalpy of mixing and depends on the intermolecular forces. EUNIQUAC Models are expressed as follows for an equilibrium system [16-17]:

$$G^E = G^E_{combinatorial} + G^E_{Residual} + G^E_{Debye-Huckel} \quad (1)$$

$$\frac{G^E_{combinatorial}}{RT} = \sum x_i \ln \left(\frac{\phi_i}{x_i} \right) - \frac{z}{2} \sum q_i x_i \ln \left(\frac{\phi_i}{\theta_i} \right) \quad (2)$$

In the upper equation, G^E is Gibbs free energy. In eq. 2, z is coordination number and its value is equal to 10; x_i is mole fraction; ϕ_i is volume fraction and θ_i is the surface area fraction of ions in the liquid-solid or liquid-vapor equilibrium system which is expressed as:

$$\phi_i = \frac{x_i r_i}{\sum x_i r_i} \quad (3)$$

$$\theta_i = \frac{x_i q_i}{\sum x_i q_i} \quad (4)$$

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:

$$\frac{G^E_{Residual}}{RT} = -\sum_i q_i x_i \ln \left(\sum_k \theta_k \phi_{ki} \right) \quad (5)$$

$$\phi_{ij} = \exp \left(-\frac{u_{ij} - u_{ii}}{T} \right) \quad (6)$$

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

$$u_{ij} = u_{ij}^o + u_{ij}^t (T - 298.15) \quad (7)$$

u_{ij}^o and u_{ij}^t are two adjustable parameters for energy interaction between the ions in the equilibrium system. The Debye-Hückel contribution (to the excess Gibbs energy) of the extended UNIQUAC model is given by the expression:

$$\frac{G^E_{Debye-Huckel}}{RT} = -x_w M_w \frac{4A}{b^3} \left[\ln \left(1 + bI^{\frac{1}{2}} \right) - bI^{\frac{1}{2}} + \frac{b^2 I}{2} \right] \quad (8)$$

Where, M_w is the molar mass of water, x_w is the mole fraction of water, A is a Debye-Hückel parameter, b is a constant equal to 1.5 (kg mol⁻¹)^{1/2}, and I is the ionic strength.

$$A = a_0 + a_1(T-273.15) + a_2(T-273.15)^2 \quad (9)$$

$$I = 0.5 \sum m_i z_i^2 \quad (10)$$

In equation, z_i is the charge of ion i and m_i is the molality (mol (kg H₂O)⁻¹) of ion i . Considering the relationship between excess Gibbs free energy and basic equations of thermodynamics, by differentiation of equations 1 with respect to the mole fraction of different species, the activity coefficient for each ion is derived:

$$\ln \gamma_i = \left[\frac{\partial \left(\frac{nG^E}{RT} \right)}{\partial n_i} \right] \quad (11)$$

$$\ln \gamma_i = \ln \gamma_i^{Residual} + \ln \gamma_i^{combinatorial} + \ln \gamma_i^{Debye-Hückel} \quad (12)$$

Finally, activity coefficient for water can be expressed as

$$\ln \gamma_w^* = \ln \left(\frac{\phi_w}{x_w} \right) + 1 - \frac{\phi_w}{x_w} - \frac{z}{2} \cdot q_w \left[\ln \left(\frac{\phi_w}{\theta_w} \right) + 1 - \frac{\phi_w}{\theta_w} \right] + q_w \left[1 - \ln(\sum_k \theta_k \phi_{kw}) - \sum_k \frac{\theta_k \phi_{wk}}{\sum \theta_l \phi_{lk}} \right] - q_i [1 - \ln(\phi_{wi}) - \phi_{iw}] + Mw \cdot \frac{2A}{b^3} \cdot \left[1 + bI^{0.5} - \frac{1}{1+bI^{0.5}} - 2\ln(1 + bI^{0.5}) \right] \quad (13)$$

RESULTS AND DISCUSSION

In this research, the described flowchart (Figure 1) has brought very good results after running the application for solution $ACl_{x=1,2}$; $A=Li,H,Na,K,NH_4,Cs,Mg,Ca, Ba$ and $B_{j=1,2}SO_4$; $B=Li,Na,K,NH_4,Mg,Mn,Ni,Cu,Zn$ and $NaCl+LaCl_{3(aq)}$, $NaCl+MgCl_{2(aq)}$, $Na_2SO_4+MgSO_{4(aq)}$ and Temperature changes 298.15 k; that the total error based on defined error equation in table 1 is reported. Figure2 show, Comparison between Water Activity values predicted by model and experimental data for aqueous chloride solutions. Based on the results this figure2, the water activity, decreased with increasing concentration (aqueous chloride solutions).

Table 2 show Comparison between water activity values predicted by model and experimental data for aqueous Sulfate solutions. Based on the results this Table2, the water activity, decreased with increasing concentration (aqueous sulfate solutions).

In table 3 is reported, Comparison between Water Activity values predicted by model and experimental data for aqueous solutions, $NaCl+LaCl_{3(aq)}$, $NaCl+MgCl_{2(aq)}$, $Na_2SO_4+MgSO_{4(aq)}$. Based on the results this Table3, the water activity, decreased with increasing concentration aqueous solutions. The results of study is confirmed accuracy and desirable capability, optimized Extended UNIQUAC model.

Table 1: Total error based on defined error equation for electrolyte solutions using Genetic algorithm

System	Error
LiCl+H ₂ O	0.0168
HCl+H ₂ O	0.013
NaCl+H ₂ O	0.0078
KCl+H ₂ O	0.00237
NH ₄ Cl+H ₂ O	0.016
CsCl+H ₂ O	0.0029
MgCl ₂ +H ₂ O	0.04
CaCl ₂ +H ₂ O	0.05
BaCl ₂ +H ₂ O	0.0045
Li ₂ SO ₄ +H ₂ O	0.0022
Na ₂ SO ₄ +H ₂ O	0.00156
K ₂ SO ₄ +H ₂ O	0.00017
(NH ₄) ₂ SO ₄	0.0045
MgSO ₄ +H ₂ O	0.005
MnSO ₄ +H ₂ O	0.0138
NiSO ₄ +H ₂ O	0.00146
CuSO ₄ +H ₂ O	0.000473
ZnSO ₄ +H ₂ O	0.0069
NaCl+LaCl ₃ +H ₂ O	0.006
NaCl+MgCl ₂ +H ₂ O	0.0086
Na ₂ SO ₄ +MgSO ₄ +H ₂ O	0.0038

Table 2: Comparison between Water Activity values predicted by model and experimental data for aqueous Sulfate solutions (Experimental reference [19])

Li₂SO₄(molar)	a_w calc	a_w exp	Na₂SO₄(molar)	a_w calc	a_w exp	K₂SO₄(molar)	a_w calc	a_w exp
0.1	0.9962	0.9956	0.1	0.9965	0.9957	0.1	0.9959	0.9958
0.2	0.992	0.9915	0.2	0.9928	0.992	0.2	0.992	0.992
0.3	0.9877	0.9875	0.3	0.9892	0.9882	0.3	0.9883	0.9884
0.4	0.9834	0.9833	0.4	0.98559	0.9848	0.4	0.98474	0.985
0.5	0.9789	0.9793	0.5	0.98196	0.9815	0.5	0.98132	0.9815
0.6	0.9744	0.953	0.6	0.9784	0.9781	0.6	0.9781	0.9783
0.7	0.97	0.971	0.7	0.97498	0.9749	0.7	0.9751	0.975
0.8	0.9651	0.9667	0.8	0.9715	0.9718	0.8	0.97222	0.972
1	0.9557	0.9585	1	0.964757	0.966			
1.5	0.9316	0.935	1.5	0.9484	0.95			
2	0.907	0.911	2	0.9327	0.935			
2.5	0.881	0.883	2.5	0.91765	0.918			
3	0.8574	0.853	3	0.9033	0.899			
(NH₄)₂SO₄(molar)	a_w calc	a_w exp	MgSO₄(molar)	a_w calc	a_w exp	MnSO₄(molar)	a_w calc	a_w exp
0.1	0.996	0.9959	0.2	0.9963	0.996	0.2	0.99469	0.9961
0.2	0.9922	0.9921	0.3	0.99417	0.9941	0.3	0.9921	0.9945
0.3	0.9883	0.9886	0.4	0.991754	0.9924	0.4	0.9893	0.9929
0.4	0.9844	0.9853	0.5	0.98943	0.9906	0.5	0.9867	0.9913
0.5	0.9805	0.982	0.6	0.9869	0.9888	0.6	0.9841	0.9898
0.6	0.9767	0.9788	0.7	0.984413	0.987	0.7	0.9815	0.9882
0.7	0.973	0.9756	0.8	0.9817	0.9851	0.8	0.978768	0.9866
0.8	0.9693	0.9724	0.9	0.9791	0.9832	0.9	0.97614	0.985
1	0.96196	0.9662	1	0.976	0.9812	1	0.97359	0.9832
1.5	0.9441	0.95	1.2	0.9709	0.9768	1.2	0.96835	0.9794
2	0.92685	0.935	1.4	0.965362	0.9717	1.4	0.9631	0.975
2.5	0.9103	0.919	1.6	0.959781	0.966	1.6	0.9581	0.9703
3	0.894357	0.902	1.8	0.95405	0.9598	1.8	0.953	0.9649
3.5	0.88	0.885	2	0.948205	0.9529	2	0.94777	0.959
4	0.864	0.867	2.5	0.93376	0.932	2.5	0.93514	0.941
4.5	0.8497	0.85	3	0.9194	0.905	3	0.92266	0.919
5	0.8354	0.831				3.5	0.9104	0.892
						4	0.898164	0.862
NiSO₄(molar)	a_w calc	a_w exp	CuSO₄(molar)	a_w calc	a_w exp	ZnSO₄(molar)	a_w calc	a_w exp
0.2	0.9985	0.9962	0.2	0.9964	0.9963	0.2	0.995	0.9962
0.3	0.99684	0.9946	0.3	0.99476	0.9947	0.3	0.993	0.9946
0.4	0.99504	0.9931	0.4	0.9929	0.9932	0.4	0.9906	0.993
0.5	0.99336	0.9916	0.5	0.99135	0.9917	0.5	0.9884	0.9914
0.6	0.99154	0.9901	0.6	0.98961	0.9901	0.6	0.986	0.9898
0.7	0.98744	0.9887	0.7	0.98794	0.9885	0.7	0.984	0.9882
0.8	0.98778	0.9871	0.8	0.98614	0.9868	0.8	0.9814	0.9865
0.9	0.985807	0.9855	0.9	0.98442	0.9851	0.9	0.9792	0.9847
1	0.983813	0.9838	1	0.98277	0.9833	1	0.97699	0.9828
1.2	0.979413	0.98	1.2	0.979314	0.9795	1.2	0.9725	0.9788
1.4	0.97462	0.9758	1.4	0.97586	0.975	1.4	0.9681	0.9743
1.6	0.9695	0.971				1.6	0.96378	0.9692
1.8	0.964	0.965				1.8	0.9594	0.9634
2	0.95787	0.9588				2	0.9551	0.957
2.5	0.94135	0.939				2.5	0.9445	0.938
						3	0.93425	0.913

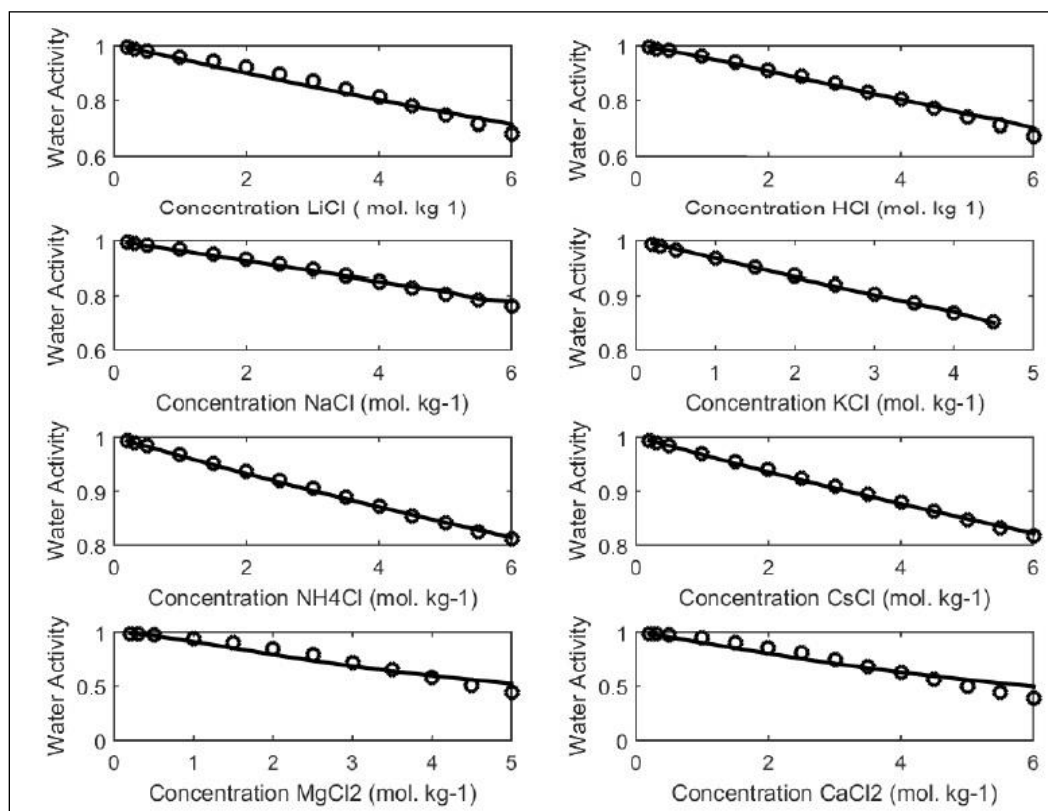


Figure 2: Comparison between Water Activity values predicted by model and experimental data for aqueous chloride solutions (Experimental reference [18])

Table3: Comparison between Water Activity values predicted by model and experimental data for aqueous solutions

NaCl (molar)	MgCl ₂ (molar)	a _w calc	a _w exp [20]	Na ₂ SO ₄ (molar)	MgSO ₄ (molar)	a _w calc	a _w exp [20]	NaCl (molar)	LaCl ₃ (molar)	a _w calc	a _w exp [21]
0.3	0.3	0.962	0.97	0.3	0.3	0.9821	0.986	2.6463	0.3677	0.87	0.869
0.6	0.2	0.9604	0.97	0.25	0.35	0.984	0.986	2.317	0.322	0.8966	0.8886
0.45	0.45	0.954	0.962	0.2	0.55	0.984	0.986	2.2931	0.1899	0.917	0.903
0.8	0.2	0.953	0.962	0.45	0.2	0.9765	0.981	1.5088	0.5162	0.904	0.903
0.65	0.51	0.943	0.949	0.3	0.42	0.981	0.981	1.3795	0.7005	0.887	0.8886
1	0.25	0.945	0.949	0.2	0.7	0.982	0.981	4.189	0.347	0.806	0.7997
1.2	0.24	0.942	0.949	0.55	0.3	0.971	0.974	2.6812	0.5858	0.84077	0.8409
0.8	0.76	0.928	0.921	0.45	0.6	0.972	0.974	2.1382	1.0858	0.7994	0.7997
1.4	0.45	0.929	0.921	0.25	0.9	0.978	0.974	1.8046	0.9164	0.83838	0.8409
1.6	0.3	0.93	0.921	0.8	0.45	0.959	0.951	1.1831	0.9399	0.86742	0.869

CONCLUSION

In this study, in order to predict the activity coefficient of electrolyte system, 21 aqueous solutions has been studied. For this study, the Extended UNIQUAC Model, has been considered and adjustable parameters with genetic algorithm has been optimized. Results of the optimization good match, Extended UNIQUAC model the experimental results based on genetic algorithms is emphasized. Based on the results this work, the water activity, decreased with increasing concentration aqueous solutions ($ACI_{x=1,2}$; $A=Li,H,Na,K,NH_4,Cs,Mg,Ca,Ba$ and $B_{j=1,2}SO_4$; $B=Li,Na,K,NH_4,Mg,Mn,Ni,Cu,Zn$ and $NaCl+LaCl_{3(aq)},NaCl+MgCl_{2(aq)},Na_2SO_4+MgSO_{4(aq)}$). These results in this study give attentions to the importance and priority of choosing optimized Extended UNIQUAC model to assess the inorganic saturation index.

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Parameter optimization (Extended UNIQUAC model) by algorithms such as Particle swarm optimization is recommended.

REFERENCES

- [1] GS Choudhury; Le Maguer. Prediction of water activity in glucose solution using the UNIFAC model. In: M. Le Maguer and P. Jelen (Eds.), Food Engineering and Process Applications. Elsevier, New York. **1986**.
- [2] Z Ha ; CK Chen. *Aerosol Science and Thechology.*, **1991**, 31, 154-169.
- [3] W Wang ; D Zeng ; H Zho ; X Wu ; X Yin. *Chem. Eng. Data.*, **2015**, 60 (10), 3024-3032.
- [4] Y Kawaguchi ; H Kanai ; H Kajiwara ; Y Arai. *J. Chem. Eng. Jpn.*, **1981**, 14, 243-246.
- [5] Y Kawaguchi ; H Kanai ; H Kajiwara ; Y Arai. *J. Chem. Eng. Jpn.*, **1982**, 15, 62-63.
- [6] A Correa ; F Comesafia ; A.M Sereno, A.M. Prediction of water activity in non-electrolyte solutions by ASOG group contribution method. Communication to CHEMPOR'93 International Chemical Engineering Conference, Porto, Portugal. **1993**.
- [7] A Apelblat; E Korin. *J Chem Thermodyn.*, **1998**, 30, 59-71.
- [8] N Hubert; Y Gabes, JB Bourdet; L Schuffenecker. *J Chem Engg Data.*, **1995**, 40, 891-894.
- [9] RA Robinson; J.B Macakill. *Journal of Soluation Chemistry.*, **1979**, 8, 35-40.
- [10] CE Taylor. *J Phys Chem-US*, **1955**, 59, 653-656
- [11] JT Moore; WT Humphries ; CS Patterson. *J Chem Engg Data.*, **1972**, 10, 323-325.
- [12] KL Hellams; CS Patterson ; BH Prentice ; MJ Taylor. *J Chem Engg Data.*, **1965**, 10, 323-325.
- [13] BA Soldano; C.S Patterson. *J Chem Society.*, **1962**, 937-940.
- [14] K Thomsen; P Rasmussen. *Chem Engg Sci.*, **1999**, 54, 1787-1802.
- [15] D Abrams; J Prausnitz. *AIChE J.*, **1975**, 21(1), 116-128.
- [16] B Sander; P Rasmussen ; Aa Fredenslund. *Chem Engg Sci.*, **1986**, 41, 1197-1202.
- [17] A Garcia; K Thomsen; E Stenby. *Geothermics.*, **2005**, 34, 61-97.
- [18] El Guendouzi; A Dinane; A Mounir. *J. Chem. Thermodyn*, **2001**, 33, 1059-1072.
- [19] El Guendouzi; A Mounir; A Dinane. *J. Chem. Thermodyn*, **2003**, 35, 209-220.
- [20] Y Wu. Y ; RM Rush ; G Scatchard. *J PhysChem.*, **1968**, 72(12), 4048-4057.
- [21] F Enzi; T Tran; T Eng. *Can. J. Chem*, **1975**, 53, 3133-3140.