

Investigation and Studying of Mineral Scale Formation Point in NaCl , Na₂SO₄, CaSO₄ Aqueous Solutions by Modified UNIFAC–Dortmund Model.

L.Yousefi,

Department of Science, Islamshahr Branch, Islamic Azad University.

Corresponding author: L.Yousefi, e-mail: ah_usefy@yahoo.com .
Tel:+98-21-44328715.

Abstract

In this work, calculation of saturation molality in saline solutions, the prediction of the mean ionic activity coefficients (MIAC) of electrolytes was done by for a number of single salt electrolyte solutions at 1 atmospheric pressure, and temperature range of 20 to 80 °C. MIAC was composed of two parts: the long – range electrostatic interaction contribution and the short - range electrostatic interaction contribution. Long range (MIAC) was represented by Debye – Hückel. It was computed by Pitzer model and pitzer interaction parameters. Modified UNIFAC–Dortmund model was used for calculation of short -range (MIAC).The data base was included 13 experimental points in each binary systems [(NaCl/H₂O), (Na₂SO₄/H₂O), (CaSO₄/H₂O)], that was used in the calculation of interaction group and in the test of predictions.

Keywords: *Electrolyte solutions; Activity coefficients; Saturation molality; Product solubility*

Introduction

One of the important challenges in the water injection process in oil wells is the incompatibility of the injection water and the connate water, that can be the cause of scale formation and obstruction in the oil matrix porous medium[1].This phenomena considerably decreases the injection and the oilfield production rates[2]. The prediction of the scale formation is a basic step toward the prevention of this problem. In this article, a reliable thermodynamic model is needed to calculate mineral solubility in single salt electrolytes, under conditions of various brine composition and temperature. The basic idea is to combine a local composition g^E model for the activity coefficient, and used it for the representation of the short-range interactions between ions and solvents, with Debye-Hückel term[3]for the long-range ion-ion electrostatic interactions.

Thermodynamic Modeling

The basic idea for electrolyte solution activity coefficient calculation is sum of the short - range and long - range interaction parts [4], as follows :

$$\ln \gamma_i^m = \ln(\gamma_i^m)_{LR} + \ln(\gamma_i^m)_{SH} \quad (1)$$

Long-range term is estimated by Debye-Hückel, Pitzer model [4, 5]. Short – range term is estimated by modified UNIFAC–Dortmund model [6].The basic idea stems from the expression of the activity coefficient as the sum of a combinatorial and a residual part, as

follows:

$$\ln(\gamma_i^m)_{SH} = \ln \gamma_i^C + \ln \gamma_i^R \quad (2)$$

Combinatorial part equations take the following forms:

$$\ln \gamma_i^C = \ln \left(\frac{\Phi_i}{X_i} \right) + 1 - \frac{\Phi_i}{X_i} - 5 q_i \left[1 - \left(\frac{\Phi_i}{\theta_i} \right) + \ln \left(\frac{\Phi_i}{\theta_i} \right) \right] \quad (3)$$

$$\Phi_i = \frac{X_i r_i^{\frac{5}{2}}}{\sum_j X_j r_j^{\frac{5}{2}}} \quad (4)$$

$$\Phi_i = \frac{X_i r_i}{\sum_j X_j r_j} \quad (5)$$

$$\theta_i = \frac{q_i X_i}{\sum_j q_j X_j} \quad (6)$$

$$r_i = \sum_k v_k^i R_k \quad (7)$$

$$q_i = \sum_k v_k^i Q_k \quad (8)$$

In Eq. (7) and (8), v_k^i is the number of subgroups in one component. Additionally; the group contributions R_k and Q_k for the molecular Vander Waals volumes and surface areas; respectively [7-9]. The residual part is given by the solution-of-groups concept, expressed by:

$$\ln \gamma_i^R = \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \quad (9)$$

In this equation, Γ_k is the group residual activity coefficient and Γ_k^i is the group residual activity coefficient for a reference solution of pure (i), which can be calculated by:

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right] \quad (17)$$

The residual part, therefore, remains unchanged comparing to the original UNIFAC, except for the fact that the energy parameter, ψ_{mn} , is corrected by a more complex expression for the temperature dependence:

$$\psi_{mn} = \exp \left(- \frac{a_{mn} + b_{mn} T}{T} \right) \quad (18)$$

Parameters a_{mn} and b_{mn} in the above expression have been fitted in this work using solid-liquid equilibrium data and activity coefficients. After MIAC was calculated by modeling

part, for calculation of m_i^{cal} was used according to the following relations:

$$m_i^{cal} = (1/\gamma_{\pm}^{(m)}) [k_{sp} / (v_+^{v_+} v_-^{v_-} (a_{H_2O})^n)]^{1/v} \quad (19)$$

Where a_{H_2O} the water activity is related to the osmotic coefficient, n the number of water molecules that have been hydrated solid salt molecules. In this work solids are anhydrous then n is zero and the calculation of water activity is not important k_{sp} is the solubility product [10-12].

Results and discussion

Fig.1,2 and 3 show the variation of the saturation molality for the single aqueous NaCl, Na₂SO₄ and CaSO₄ electrolyte solutions as a function of temperature obtained from this work (model), and literature(lit.) models and experimental (exp.) at 1 atm.

Table1 present the regressed values for the binary interaction parameters introduced in the model along. The adjustable parameters given in Table 1 were regressed using the experimental data for saturation molality of the single aqueous electrolyte solutions in the temperature range of 20 - 80°C. It should be stated that to obtain the regressed parameters the following objection function was minimized:

$$OBJ = \frac{1}{np} \sum_i^{np} (\gamma_i^{exp} - \gamma_i^{cal})^2 \quad (20)$$

Where **np** refers to the number of the experimental data points, γ_i^{exp} and γ_i^{cal} are respectively the experimental and calculated mean ionic activity coefficients of the single salt electrolyte at saturated solution.

Conclusion

In this work, solid–liquid equilibrium data were predicted for 3 binary solvent–salt systems [(NaCl/H₂O), (Na₂SO₄/H₂O), (CaSO₄/H₂O)] at 1 atmospheric pressure in the temperature range of the 20–80 °C. The Debye- Hückel, Pitzer model and pitzer interaction parameters was used for calculation of long-range mean ionic activity coefficient. The Modified UNIFAC–Dortmund model was used for calculation of short-range mean ionic activity coefficient. Mineral scale formation in single salt electrolyte solutions that is the same saturation molality of single salt electrolyte solutions was predicted. The results are shown in the form of experimental, predicted by this work model and literature values of the molality (saturation molality of single salt electrolyte solutions) for the special temperature range. These results are very satisfactory, considering that Modified UNIFAC–Dortmund is a group contribution predictive method.

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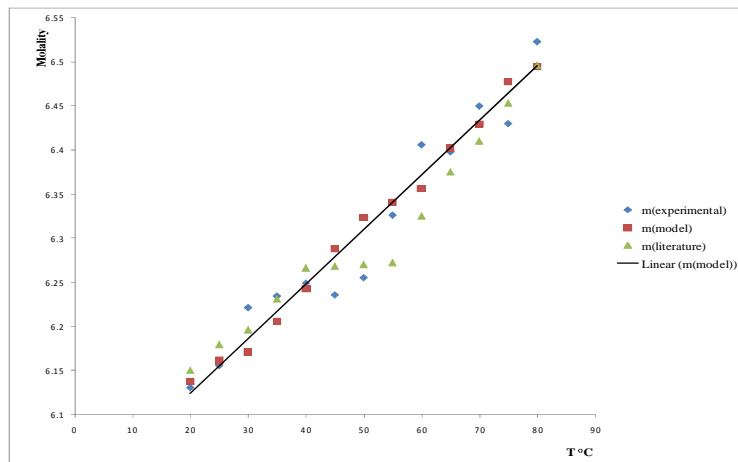


Fig.1.Saturation molality of NaCl in water at 1 atmospheric pressure as a function of temperature.

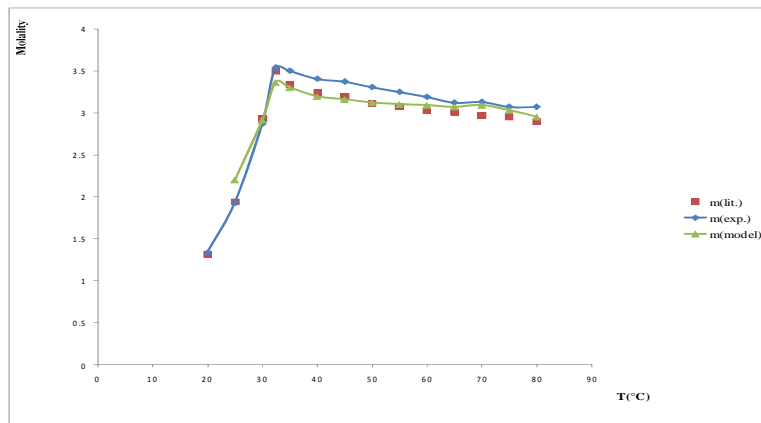


Fig.2. saturation molality of Na₂SO₄ in water at 1 atmospheric pressure as a function of temperature.

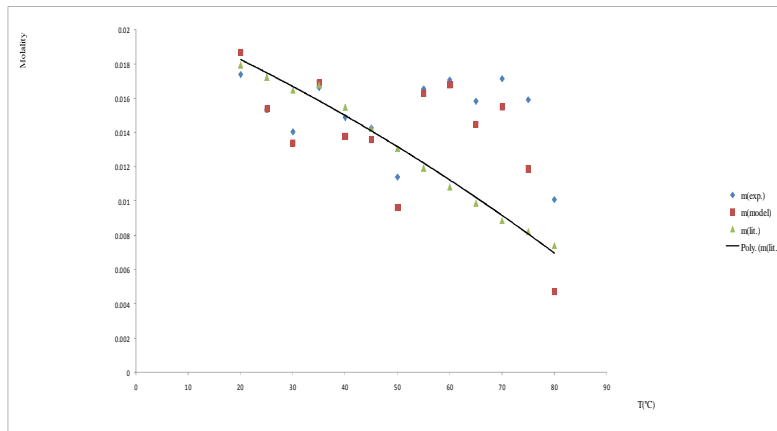


Fig. 3. Saturation molality of CaSO_4 in water at 1 atmospheric pressure as a function of temperature.

Table1. Regressed parameters to represent ion-ion and ion-water interactions.

i	j	a_{ij}	a_{ji}	b_{ij}	b_{ji}
H_2O	H_2O	-0.0586	-0.0586	-0.3051	-0.3051
H_2O	Na^+	160.4559	-0.0032	-2.1723	-0.058
H_2O	Cl^-	0.5009	0.0068	1.5564	2.3021
H_2O	SO_4^{2-}	-3092.038	15648.2948	12.16175	-44.29628
H_2O	Ca^{2+}	320.75948	-2051.6128	0.01943	-512
Na^+	Na^+	0.0296	0.0296	-0.051	-0.051
Na^+	Cl^-	0.0228	4.3073	0.2879	-0.0403
Na^+	SO_4^{2-}	295.1469	3.767	0.08911	1.3101
Cl^-	Cl^-	0.5216	0.5216	-0.0258	-0.0258
SO_4^{2-}	SO_4^{2-}	18.75501	18.75501	0.93212	0.93212
SO_4^{2-}	Ca^{2+}	-877.1016	-212.01953	-4.00791	-2.92969
Ca^{2+}	Ca^{2+}	-0.0001	-0.0001	1024.0001	1024.0001