The prediction of the amount of salt sediment in the electrolyte solutions with the extended equation of states based on Peng Robinson equation of state

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ABSTRACT

The solubility of several salt in different electrolyte solutions is modeled by using the proposed equation of state. The modified Peng-Robinson equation of state, Born and MSA terms, were used at this model. To do this modeling, a large number of experimental data has been collected for electrolyte systems. At this modeling, optimization based on salt has used and van der Waals attraction parameter, van der Waals excluded-volume parameter, ion diameter and binary interaction parameter between the molecule-salt have been optimized by fitting experimental data of liquid density and average mean ionic activity coefficients over wide range of temperatures. The Average relative deviation for prediction of salt solubility in the electrolyte solutions, for potassium dichromate solution, potassium chlorate solution, potassium nitrate solution, ammonium chloride solution, sodium sulfate solution, potassium iodide solution, sodium nitrate solution, potassium sulfate solution is obtained 2.23% ,1.16% ,1.28% ,1.93 %, 1.34 %, 2.28%, 2.57%, 1.03% respectively. The solubility of three-component systems were also predicted with good accuracy. The solubility of salts in ternary systems was also predicted with high accuracy. The results showed that this model could predict solid-liquid equilibrium behavior over a wide range of temperature and pressure.

Keywords: *Electrolyte solutions, Equation of states, Peng Robinson, Salt sediment, Salt Sediment , Solid- liquid equilibrium.*

1. *INTRODUCTION*

Electrolyte solutions play an important role in many industrial and natural processes. In geology, electrolytes have an effect on many processes such as the conversion of contaminated water treatment, the flow of contaminated underground water and the production of underground energy. In many processes, such as desalination, purification of polluted water, distillation, extraction, and investigation of deposits in gas transmission pipes, understanding the equilibrium state of electrolyte systems is very necessary and important. [1]

For gas sweetening, the use of amine solvent to separate carbon dioxide and sulfur dioxide is necessary to understand the phase equilibria of electrolyte systems. In oil and gas production, it is necessary to check the balance of systems containing electrolytes to prevent hydrate formation, prevent corrosion, prevent precipitation problems, and increase oil recovery [2].

Many different models have been proposed to describe the thermodynamic properties of electrolyte solutions. About the solid-liquid equilibrium in electrolyte solutions compared to the vapor-liquid equilibrium, few related studies have been done [2, 3].

Farelo and his colleagues developed a simple algorithm for salt solubility in binary and ternary systems of NaCl, KCl and H_2O in the temperature range of 293 to 360 K by applying Pitzer's pseudo-theoretical *equation for excess Gibbs energy [4]. Kolker and Pablo proposed a semi-empirical thermodynamic model for predicting the solubility of semi-organic mixed salt using experimental data of pure substance and infinitely dilute substance [5]. Tan et al.'s electrolyte equation of state includes the SAFT equation of state plus an MSA finite element model for ionic interactions [6].*

2. *Theory and relationships used in the article*

The pressure equation is shown by the following relation:

$$P=f(T,V,\bar{n}) \qquad (1)$$

The pressure is obtained from the derivative of the Helmholtz free energy with respect to the volume as follows:

$$P=-\left(\frac{\partial A(T,V,\bar{n})}{\partial V}\right)_{T,\bar{n}} \qquad (2)$$

In the above relationship, (V) is the total volume, (n) is the number of moles of the mixture components and (T) is the temperature of the system. The fugacity coefficient of the components is obtained by the following equation:

$$RT\ln\emptyset_i=\left(\frac{\partial A_{nonionic}}{\partial n_i}\right)_{T,V,n_i\neq n_j}+\left(\frac{\partial A_{ionic}}{\partial n_i}\right)_{T,V,n_i\neq n_j}-RT\ln Z \qquad (3)$$

The chemical potential of the species in the solution is also determined using the following equation:

$$\mu_i(T,P,\bar{x})=\left(\frac{\partial A(T,V,\bar{n})}{\partial n_i}\right)_{T,V,n_i\neq n_j} \qquad (4)$$

Electrolytic state equations for electrolyte solutions are expressed relationally based on the remaining Helmholtz free energy. These equations consist of two main parts. The first part contains an expression for non-electrolyte components and the second part contains an expression for electrolyte components:

$$\left(\frac{A^r}{RT}\right)=\left(\frac{A^r}{RT}\right)_{non-Electrolyte}+\left(\frac{A^r}{RT}\right)_{Electrolyte} \qquad (5)$$

The electrolyte part of the equation of state includes MSA and Born terms.

$$\left(\frac{A^r}{RT}\right)_{Electrolyte}=\left(\frac{A^r}{RT}\right)_{MSA}+\left(\frac{A^r}{RT}\right)_{Born} \qquad (6)$$

In this work, the explicit simplified equation of MSA is used.

$$a_{MSA}=-\frac{2\Gamma^3RTv}{3\pi N_A}\left(1+\frac{3}{2}\sigma\Gamma\right) \qquad (7)$$

N_A *is Avogadro's number, e is electron charge,* ε_0 *is electric conductivity in vacuum,* Z_i *is ion charge number, v is molar volume. k is the Debye length, Γ is the screening parameter and σ is the average diameter of the ions, which are determined using the following relations:*

$$k^2=\frac{e^2N_A^2}{D\varepsilon_0RTv}\sum_{ions}x_iZ_i^2 \qquad (8)$$

$$\Gamma = \frac{1}{2\sigma}\left[\sqrt{1+2\sigma k}-1\right] \tag{9}$$

$$\sigma = \frac{\sum x_i \sigma_i}{\sum x_i} \tag{10}$$

D_s is the dielectric constant of the pure solvent and D is the dielectric constant of mixed solvents and is calculated from the following equation:

$$D = \frac{\sum x_s D_s}{\sum x_s} \tag{11}$$

If water is the solvent in electrolytic solutions, D will be equal to D_s. Dielectric constant for a pure solvent as a function of temperature is obtained from the following equation:

$$D_s = d_0 + \frac{d_1}{T} + d_2 T + d_3 T^2 + d_4 T^3 \tag{12}$$

The pressure equation and the chemical potential of the MSA sentence are obtained from the following relations:

$$P_{MSA} = \frac{2\Gamma^3 RT}{3\pi N_A}\left(1+\frac{3}{2}\sigma\Gamma\right) - \frac{RTk^2}{4\pi N_A}\frac{\Gamma}{1+\sigma\Gamma} \tag{13}$$

$$\frac{\mu_{i,MSA}}{RT} = \frac{e^2 N_A}{4\pi D \varepsilon_0 RT}\frac{\Gamma}{1+\sigma\Gamma}\left(-Z_i^2 + \frac{1}{D}\frac{\partial D}{\partial n_i}\sum_{ion} n_i Z_i^2\right) \tag{14}$$

For water, $\frac{\partial D}{\partial n_i}$ is written as follows:

$$\left(\frac{\partial D}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \frac{1}{n_t}\frac{D_S - D}{\sum_s x_s} i \tag{15}$$

It should be noted that for ions and acid gases, $\frac{\partial D}{\partial n_i}$=0 [7].

Another term added in the electrolyte section of the Helmholtz free energy equation is Born's term. The remaining Helmholtz Borne energy contribution is expressed by the following equation:

$$a_{Born} = -\frac{N_A e^2}{4\pi\varepsilon_0}\left(1-\frac{1}{D}\right)\sum_{ions}\frac{x_i Z_i^2}{\sigma_i} \tag{16}$$

Equations of pressure and chemical potential of Born's sentence [7] are calculated using the following relations:

$$P_{Born} = 0 \tag{17}$$

$$\frac{\mu_{i,Born}}{RT} = \frac{N_A e^2}{RT 4\pi\varepsilon_0}\left(-\frac{1}{D^2}\frac{\partial D}{\partial n_i}\sum_{ions}\frac{n_i Z_i^2}{\sigma_i} - \frac{Z_i^2}{\sigma_i}\left(1-\frac{1}{D}\right)\right) \tag{18}$$

In these relationships, σ is the diameter of the particle, ε_0 is the electrical conductivity of the vacuum, R is the gas constant, and N_A is Avogadro's number.

In this research, the Peng-Robinson equation of state of Tsai and Chen [8] volume modification type is used. This equation is defined as follows:

$$\Delta A^{PR}(T,V,\bar{n}) = \frac{Na}{2\sqrt{2}b} ln\left(\frac{V+c+b(1-\sqrt{2})}{V+c+b(1+\sqrt{2})}\right) - NRTln\left(\frac{V+c-b}{V}\right) \tag{19}$$

$$c = \frac{1}{n}\sum_{i} n_i c_i \tag{20}$$

In this regard, a is called the van der Waals absorption parameter, b is the van der Waals volume parameter, and c is the volume modification parameter.
In these equations, a and b for the mixture of materials are calculated from the following relationships:

$$a = \sum\sum x_i x_j a_{ij} \tag{21}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - K_{ij}\right) \tag{22}$$

$$b = \sum b_i x_i \tag{23}$$

a_i *and* b_i *are parameters of pure components which are calculated using the following relations:*

$$a_i = \left(\frac{0.4572 R^2 T_{c,i}^2}{P_{c,i}}\right) \tag{24}$$

$$b_i = \left(\frac{0.0778 R T_{c,i}}{P_{c,i}}\right) \tag{25}$$

In Peng-Robinson equation of state, fugacity for pure compounds and for each component in a mixture are calculated respectively using the following equations:

$$ln\,\emptyset = (Z-1) - ln(Z-B) + \frac{A}{2B\sqrt{2}}\,ln\frac{Z+\left(1-\sqrt{2}\right)B}{Z+\left(1+\sqrt{2}\right)B} \tag{26}$$

$$ln\,\emptyset_i = \frac{b_i}{b}(Z-1) - ln(Z-B) - \frac{A}{B(\delta_2-\delta_1)}\left(\frac{\left(2\sum_{j=1}^{N} X_j a_{ij}\right)}{a} - \frac{b_i}{b}\right) ln\frac{Z+\delta_2 B}{Z+\delta_1 B} \tag{27}$$

which in the above relation are $\delta_1=1+\sqrt{2}$ *and* $\delta_2=1-\sqrt{2}$*[9].*

3. Calculation of activity coefficient and solubility

The activity coefficient of the pure solvent is obtained using the following equation [10]:

$$\gamma_i = \frac{\widehat{\emptyset}_i(T,P,x_i)}{\emptyset_i(T,P,x_i=1)} \tag{28}$$

The asymmetric activity coefficient is determined using the following equation:

$$\gamma_i^* = \frac{\widehat{\emptyset}_i(T,P,x_i)}{\emptyset_i(T,P,x_i\to 0)} \tag{29}$$

γ_i is used for water and γ_i^* is used for other molecules and ions.
For the soluble species, the molar activity coefficient is calculated using the following equation:

$$\gamma_i^m(T,P,\bar{n}) = \left(\frac{1}{1+\upsilon m M_{Solvent}}\right) * \left(\frac{\bar{\varphi}_i(T,P,\bar{n})}{\bar{\varphi}_i(T,P,\bar{n}_i=0)}\right) \qquad (30)$$

For an electrolyte solution containing a single salt, the average ionic activity coefficient is calculated by the following equation:

$$\gamma_\pm^m = [(\gamma_+^m)^{\upsilon+} * (\gamma_-^m)^{\upsilon-}]^{\frac{1}{\upsilon}} \qquad (31)$$

where $\upsilon+$ and $\upsilon-$ are the stoichiometric number of the cation and the stoichiometric number of the anion, respectively. υ is also the sum of the stoichiometric number of cation and anion.
To calculate the solubility of a salt such as NaCl in water, the following equation is used:

$$K_{sp,NaCl} - (\gamma_\pm^m)^2(m_{Na+}.m_{Cl-}) = 0 \qquad (32)$$

where $m_{Na+}=m_{Cl-}\approx m$ and m is the solubility in one kilogram of water at a constant temperature and in a saturated state. Having K_{sp} for NaCl and using a suitable model to calculate the average ionic activity coefficient, by trial and error, equation (32) is solved and the value of m is obtained.
The following equation is used to calculate the value of K_{sp} at different temperatures:

$$\ln K_{sp}(T) = \ln K_{sp}(T_r) - \frac{\Delta h(T_r)}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right) + \frac{\Delta C_P(T_r)}{R}\left(\ln\frac{T}{T_r}+\frac{T_r}{T}-1\right) \qquad (33)$$

At normal saturation pressures, the effect of pressure on the solubility of salts in solvents is negligible. But at high pressures, for example, 200 bar, the effect of pressure is noticeable.

4. Discussion and analysis of results

4.1. Prediction of precipitation of electrolytic solution including one electrolyte:

The specific heat capacity data were taken from the work of Roux and his colleagues [11], and the enthalpy of formation of salts and the solubility coefficient of salts at standard temperature (25 °C) were taken from the NIST database and the Chemistry Handbook [12].

To calculate the solubility, first the molality of the salt in the electrolytic solution is estimated, and by obtaining the volume of the solution, the fugacity value and the average ionic activity coefficient are calculated. Then the solubility of the salt in the electrolyte solution is calculated and finally the molality of the salt is obtained. This trial and error method continues until the difference between the new molality and the previous salt molality becomes very small. In this way, the solubility of the salt in the electrolyte solution is calculated.

The binary interaction parameters of water-salt and salt-water are considered equal. Salt-salt and water-water interactions have also been ignored. Therefore, for optimization, in different temperature ranges, the parameters of the model are a, b, and σ for salt and k_{sw} for water-salt interaction.

Average relative deviation (ARD) is defined as follows:

$$ARD\% = \frac{1}{N}\sum_{i=1}^{N}\left(\left|\frac{m_i^{experiment} - m_i^{calculated}}{m_i^{experiment}}\right|\right) * 100\% \qquad (34)$$

where $m_i^{experiment}$ *are the experimental values and* $m_i^{calculated}$ *are the calculated values of molality. Solubility experimental data are taken from sources [13-20].*

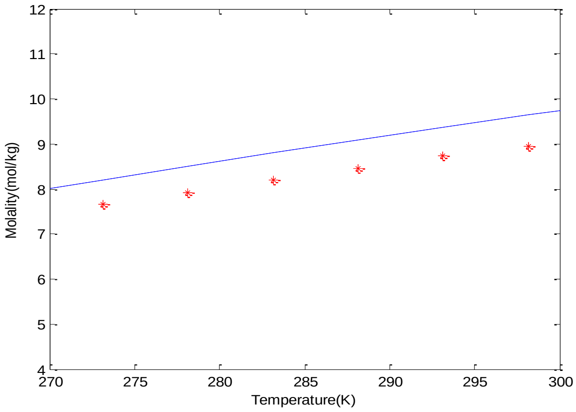

***Fig 1**. Comparison of the calculated and experimental solubility of the* $H_2O - KI$ *system at different temperatures, ARD=2.28%, laboratory data (*) and calculation data (-)*

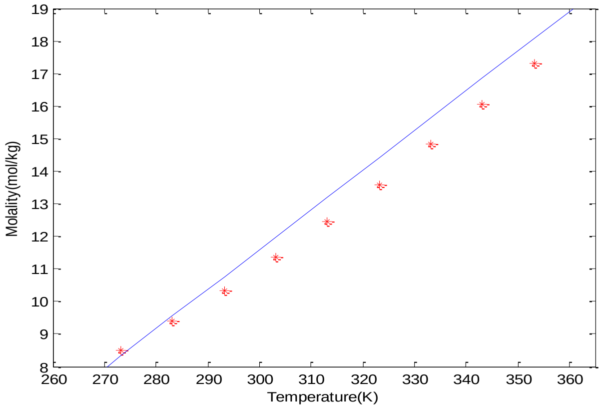

***Fig 2**. Comparison of the calculated and experimental solubility of the* $H_2O - KNO_3$ *system at different temperatures, ARD=1.28%, laboratory data (*) and calculation data (-)*

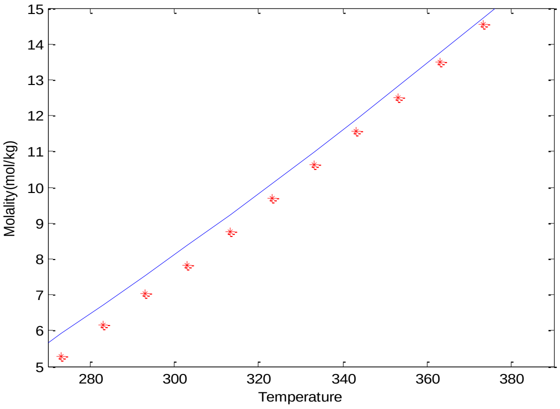

Fig 3. *Comparison of the calculated and experimental solubility of the* $H_2O - NH_4Cl$ *system at different temperatures, %ARD=1.93, laboratory data (*) and calculation data (-)*

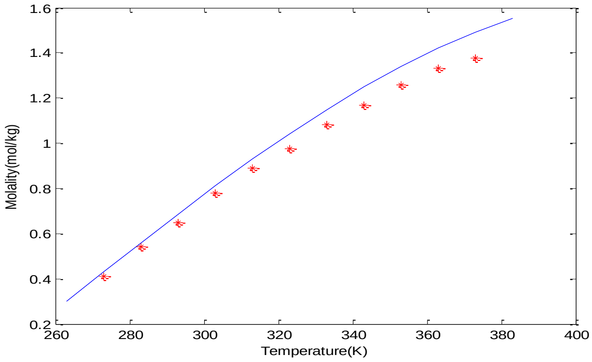

Fig 4. *Comparison of the calculated and experimental solubility of the* $H_2O - K_2SO_4$ *system at different temperatures, %ARD = 1.03, laboratory data (*) and calculation data (-)*

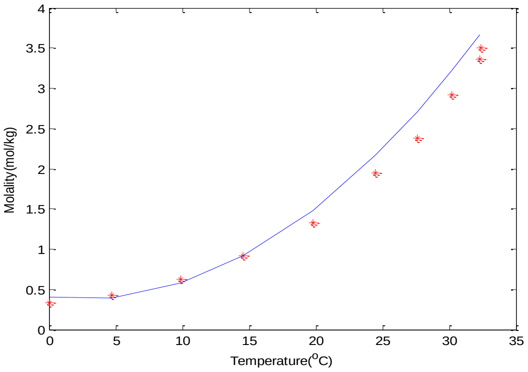

Fig 5. *Comparison of calculated and experimental solubility of* $Na_2SO_4 - H_2O$*system at different temperatures, %ARD=1.34, laboratory data(*) and calculation data(-)*

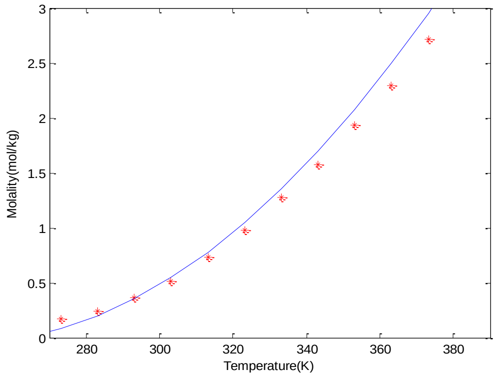

Fig 6. *Comparison of calculated and experimental solubility of* $K_2Cr_2O_7 - H_2O$ *system at different temperatures, %ARD=2.23, laboratory data (*) and calculation data(-)*

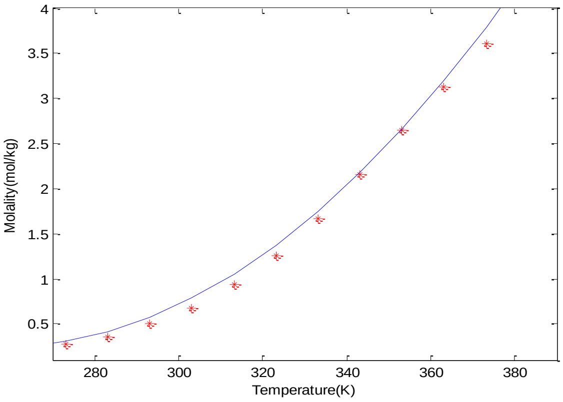

Fig 7. *Comparison of the calculated and experimental solubility of the* $KClO_3 - H_2O$ *system at different temperatures, %ARD=1.16, laboratory data (*) and calculation data (-)*

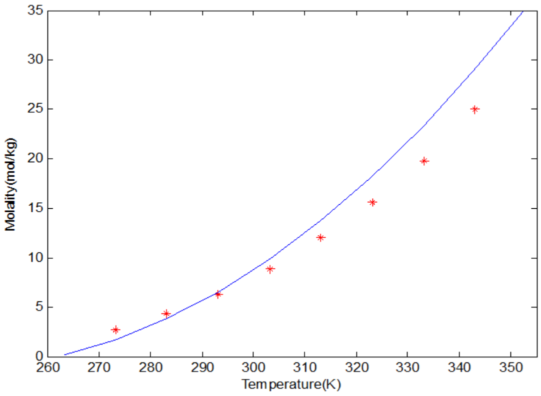

Fig 8.*Comparison of calculated and experimental solubility of* $H_2O - NaNO_3$ *system at different temperatures, ARD=2.57%, laboratory data(*) and calculation data(-)*

5. Prediction of precipitation of electrolytic solution including two electrolytes:

To predict the precipitation of salts in an electrolytic solution containing two salts, the following trial and error method is used:

First, for each hypothetical value of the molality of a salt, an initial value for the solubility of another salt is considered. Having the average ionic activity coefficient for salt, the solubility values of salt (m_1) will be obtained by guess and error.

$$K_{SP,1} - m_1(m_1 + m_2)\gamma_{\pm,1}^2 = 0 \qquad (35)$$

m_1 and m_2 refer to the molality of the first salt and the molality of the second salt, respectively. $\gamma_{\pm,1}$ is the average ionic activation coefficient and $K_{SP,1}$ is the solubility coefficient of component one at a certain temperature. The data related to the solubility of three-component systems are taken from the Handbook of Aqueous Electrolyte Thermodynamics [21].

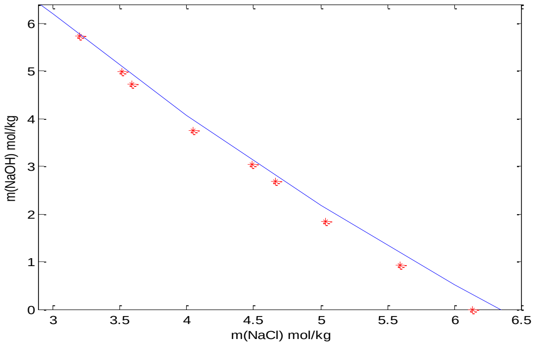

***Fig 9**. Solubility diagram of the three-component system $NaCl - H_2O - NaOH$ at 25 degrees Celsius, ARD =2.34% , laboratory data (*) and calculation data (-)*

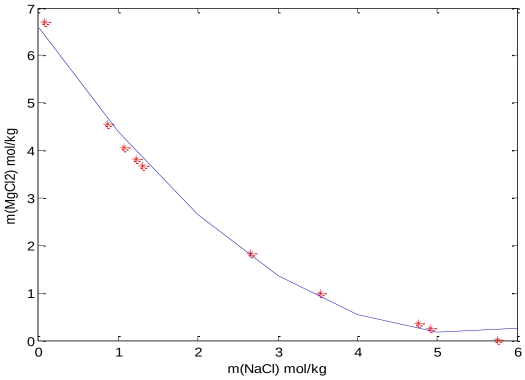

***Fig 10**. Solubility diagram of three-component system $NaCl - H_2O - MgCl_2$at 25 degrees Celsius, ARD% = 1.89, laboratory data (*) and calculation data (-)*

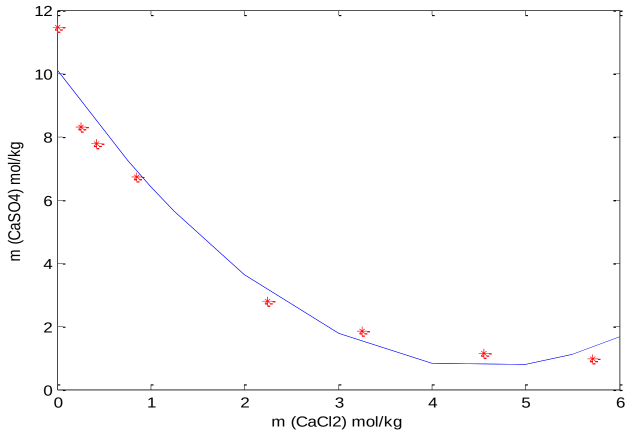

Fig 11. *Solubility diagram of three-component system $CaSO_4 - H_2O - CaCl_2$ at 25 degrees Celsius, ARD= 4.78% laboratory data (*) and calculation data (-)*

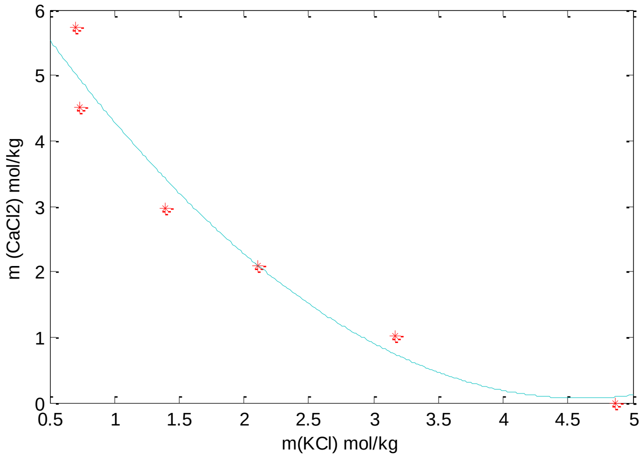

Fig 12. *Solubility diagram of the three-component system $KCl - H_2O - CaCl_2$ at 25 degrees Celsius, ARD = 3.69% ,laboratory data (*) and calculation data (-)*

5. Conclusions

In this research, the solubility of different salts in aqueous solution is modeled using the electrolytic state equation including Peng-Robinson, Born and MSA terms. For the non-electrolyte part, the modified Peng-Robinson equation of state was used by Tsai and Chen. Based on this, the parameters of the model for the pure solvent were optimized according to the experimental data of vapor pressure and liquid density. Salt-based optimization is used in this modeling.

The Average relative deviation for prediction of salt solubility in the electrolyte solutions, for potassium dichromate solution, potassium chlorate solution, potassium nitrate solution, ammonium chloride solution, sodium sulfate solution, Calcium chloride solution is obtained 2.23% , 1.16% ,1.28% , 1.93 % , 1.36 % , 3.19% respectively. The solubility of salts in ternary systems was also predicted with high accuracy. Finally, the results of this research show that this model is in good agreement with the experimental data. As a result, this model is an efficient model for the solubility of salts in aqueous solution.

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