Prediction of density and activity coefficient in electrolyte solutions

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ABSTRACT

In this article, using Peng-Robinson equation of state and Born and MSA terms, fugacity coefficient, density are predicted for electrolyte systems. In this modeling, a large amount of experimental data has been collected for electrolyte systems. In this modeling, salt-based optimization is used, and van der Waals attraction parameter, van der Waals excluded volume parameter, ion diameter parameter, and salt-molecule binary interaction parameter are optimized by fitting the experimental data of liquid density and average ion average. Average ionic activity coefficients and density in some electrolyte solutions were predicted with high accuracy .For example the Average relative deviation for prediction of average ionic activity coefficients for calcium chloride in its solution at 298.15K and 598.15K is obtained 0.71% , 1.1% respectively; and the Average relative deviation for prediction of density for Sodium bromide solution at 313.15K and 573.15K is obtained 1.75%, 3.88% respectively.

Keywords: *Electrolyte solutions, Activity coefficient, Density, Peng-Robinson , MSA, Born.*

1. *INTRODUCTION*

In many processes, such as purification of polluted water, desalination ,distillation ,extraction and checking the formation of deposits in gas transmission pipes, understanding the equilibrium state of electrolyte systems is necessary and important [1].

Choosing and using thermodynamic models of liquid-solid balance to predict salt deposition in aqueous solutions is necessary and essential for many engineering operations, for example, in the oil industry, geothermal heating, and in deposition inside heat exchangers, pipelines, and turbines. In gas and oil production, it is important to check the balance of electrolyte systems to prevent hydrate formation , prevent precipitation problems, prevent corrosion and increase oil recovery [2].

Many various 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 [3, 4].

Planche and Renon proposed an electrolyte equation of state that includes a hard spherical term and an attraction term for the interaction of all compounds and an implicit MSA term for the long-range contribution [5]. Jin and Donohue developed an electrolyte equation of state based on the PACT equation of state, which was similar to the PACT expansion for ion-ion and ion-molecule interactions [6, 7]. A generalized SRK equation of state, a specific ion attraction term, and a simplified MSA term are combined in Furst and Renon's equation of state of electrolyte [8]. Wu and Praznitz used the PR equation of state plus the aggregation term for molecule-molecule interaction. They used aggregation and Born terms for ionic interactions [9]. Galindo

and his colleagues extended the SAFT-VR model for aqueous electrolyte solution in which the simplified MSA term was used to describe the long range [10].

2. *Theory and relationships used in the article*

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:

$$\left(\frac{A^r}{RT}\right) = \left(\frac{A^r}{RT}\right)_{non-Electrolyte} + \left(\frac{A^r}{RT}\right)_{Electrolyte} \qquad (1)$$

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

$$\left(\frac{A^r}{RT}\right)_{Electrolyte} = \left(\frac{A^r}{RT}\right)_{MSA} + \left(\frac{A^r}{RT}\right)_{Born} \qquad (2)$$

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

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

N_A is Avogadro's number, e is electron charge, $\varepsilon_0$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:

$$k^2 = \frac{e^2 N_A^2}{D\varepsilon_0 RTv}\sum_{ions} x_i Z_i^2 \qquad (4)$$

$$\Gamma = \frac{1}{2\sigma}\left[\sqrt{1+2\sigma k} - 1\right] \qquad (5)$$

$$\sigma = \frac{\sum x_i \sigma_i}{\sum x_i} \qquad (6)$$

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:

$$D = \frac{\sum x_s D_s}{\sum x_s} \qquad (7)$$

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:

$$D_s = d_0 + \frac{d_1}{T} + d_2T + d_3T^2 + d_4T^3 \tag{8}$$

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

$$P_{MSA} = \frac{2\Gamma^3 RT}{3\pi N_A}\left(1 + \frac{3}{2}\sigma\Gamma\right) - \frac{RTk^2}{4\pi N_A}\frac{\Gamma}{1+\sigma\Gamma} \tag{9}$$

$$\frac{\mu_{i,MSA}}{RT} = \frac{e^2 N_A}{4\pi D\varepsilon_0 RT}\frac{\Gamma}{1+\sigma\Gamma}\left(-Z_i^2 + \frac{1}{D}\frac{\partial D}{\partial n_i}\sum_{ion} n_i Z_i^2\right) \tag{10}$$

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

$$\left(\frac{\partial D}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \frac{1}{n_t}\frac{D_S - D}{\sum_s x_s} i \tag{11}$$

It should be noted that for ions and acid gases, $\frac{\partial D}{\partial n_i}$*=0 [11].*

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:

$$a_{Born} = -\frac{N_A e^2}{4\pi\varepsilon_0}\left(1 - \frac{1}{D}\right)\sum_{ions}\frac{x_i Z_i^2}{\sigma_i} \tag{12}$$

Equations of pressure and chemical potential of Born's sentence [11] are calculated using the following relations:

$$P_{Born} = 0 \tag{13}$$

$$\frac{\mu_{i,Born}}{RT} = \frac{N_A e^2}{RT4\pi\varepsilon_0}\left(-\frac{1}{D^2}\frac{\partial D}{\partial n_i}\sum_{ions}\frac{n_i Z_i^2}{\sigma_i} - \frac{Z_i^2}{\sigma_i}\left(1 - \frac{1}{D}\right)\right) \tag{14}$$

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 [12] volume modification type is used. This equation is defined as follows:

$$\Delta A^{PR}(T,V,\bar{n}) = \frac{Na}{2\sqrt{2}b}\, ln\left(\frac{V + c + b\left(1 - \sqrt{2}\right)}{V + c + b\left(1 + \sqrt{2}\right)}\right) - NRTln\left(\frac{V + c - b}{V}\right) \tag{15}$$

$$c = \frac{1}{n}\sum_i n_i c_i \tag{16}$$

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:

$$a = \sum\sum x_i x_j a_{ij} \tag{17}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - K_{ij}\right) \tag{18}$$

$$b = \sum b_i x_i \tag{19}$$

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

$$a_i = \left(\frac{0.4572R^2T_{c,i}^2}{P_{c,i}}\right) \tag{20}$$

$$b_i = \left(\frac{0.0778RT_{c,i}}{P_{c,i}}\right) \tag{21}$$

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

$$ln\,\emptyset = (Z-1) - ln(Z-B) + \frac{A}{2B\sqrt{2}}\,ln\frac{Z+\left(1-\sqrt{2}\right)B}{Z+\left(1+\sqrt{2}\right)B} \tag{22}$$

$$ln\,\emptyset_i = \frac{b_i}{b}(Z-1) - ln(Z-B) - \frac{A}{B(\delta_2-\delta_1)}\left(\frac{\left(2\sum_{j=1}^{N}X_j a_{ij}\right)}{a} - \frac{b_i}{b}\right)ln\frac{Z+\delta_2 B}{Z+\delta_1 B} \tag{23}$$

which in the above relation are $\delta_1=1+\sqrt{2}$ and $\delta_2=1-\sqrt{2}$[13].

3. Calculation of activity coefficient

The activity coefficient of the pure solvent is obtained using the following equation [14]:

$$\gamma_i = \frac{\hat{\emptyset}_i(T,P,x_i)}{\emptyset_i(T,P,x_i=1)} \tag{24}$$

The asymmetric activity coefficient is determined using the following equation:

$$\gamma_i^* = \frac{\hat{\emptyset}_i(T,P,x_i)}{\emptyset_i(T,P,x_i\to 0)} \tag{25}$$

$\gamma_i$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:

$$\gamma_i^m(T,P,\bar{n}) = \left(\frac{1}{1+\upsilon m M_{Solvent}}\right) * \left(\frac{\bar{\varphi}_i(T,P,\bar{n})}{\bar{\varphi}_i(T,P,\bar{n}_i=0)}\right) \qquad (26)$$

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

$$\gamma_\pm^m = [\left(\gamma_+^m\right)^{\upsilon+} * \left(\gamma_-^m\right)^{\upsilon-}]^{\frac{1}{\upsilon}} \qquad (27)$$

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.

4. Discussion and analysis of results

4.1. Setting model parameters

An equation of state should be able to predict the properties of the pure material with reasonable accuracy. In the following, the process of calculations related to setting the parameters of pure water and also setting the parameters of pure salt is explained.

In the modeling of electrolytic solutions, the parameters related to the pure solvent are first obtained through optimization. Considering the terms used in this article, to check pure water, due to the absence of salt and ions, MSA and Born terms are considered equal to zero, and the only remaining term is Peng Robinson's term.

Considering the following objective function, the values of a, b, and c for pure water in the temperature range of 10°C to the critical temperature of water and pressure up to 250 bar are obtained based on the data of density and water vapor pressure.

$$Objective\ Function = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\rho_{i,exp}^{liq}-\rho_{i,calc}^{liq}}{\rho_{i,exp}^{liq}}\right| + \frac{1}{n}\sum_{i=1}^{n}\left|\frac{P_{i,exp}^{sat}-P_{i,calc}^{sat}}{P_{i,exp}^{sat}}\right| \qquad (28)$$

If vapor pressure is also considered in the objective function, the calculation of vapor pressure is obtained from the condition of equality of vapor fugacity and liquid fugacity. In this way, first the vapor pressure is guessed and then the new pressure is replaced by the previous pressure multiplied by the ratio of fugacity in the liquid phase to fugacity in the vapor phase. In this way, if the difference between the new calculated saturation pressure and the previous value is very small, the obtained pressure is the result of the calculated pressure.

The specific heat capacity data were taken from the work of Roux and his colleagues [15].

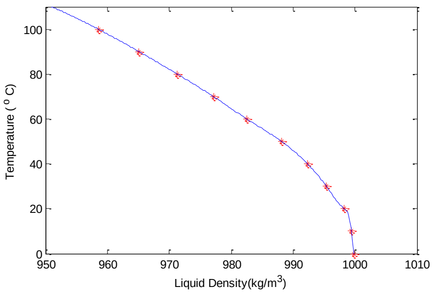

Fig 1 *.Comparison of pure water liquid density of laboratory (*) and calculation (-) data*

$\rho_{i,exp}^{liq}$ and $\rho_{i,calc}^{liq}$ are the laboratory and calculation liquid density, respectively, and $P_{i,exp}^{sat}$ and $P_{i,calc}^{sat}$ are the laboratory and calculation vapor pressure, respectively show

Using the Levenberg-Marquard algorithm used by Myers and his colleagues, the optimized parameters for pure water were obtained as temperature-dependent functions as follows.

$$a_{H_2O}\left(Pa.\frac{m^3}{mol}\right) = 1.2644 - 0.89381 * T_r + 0.16937 * T_r^2 \qquad (29)$$

$$b_{H_2O}\left(\frac{cm^3}{mol}\right) = 15.6345 + 6.14518 * T_r - 5.2795 * T_r^2 \qquad (30)$$

$$c_{H_2O}\left(\frac{cm^3}{mol}\right) = -2.7227 + 11.4201 * T_r - 6.0157 * T_r^2 \qquad (31)$$

in which:

$$T_r(k) = {}^{T}/_{647.29} \qquad (32)$$

According to the optimization results, the optimized parameters for pure water, considering the liquid density and vapor pressure at the same time, the relative deviation from the laboratory data of liquid density and vapor pressure are 0.83 and 0.22, respectively. has come.

4.2. Set salt parameters at 25°C and 1 bar pressure

For salts in electrolyte solution, MSA and Born terms become important. Therefore, adjustable parameters for salt are a, b, c, σ, and k_{ij} By assumption, the volume parameter c for salts is considered equal to zero. Also, to simplify the calculations, k_{ij} is assumed to be zero.

Therefore, parameters a, b and σ should be optimized for pure salts. These parameters have been adjusted according to the following objective function:

$$Objecive\ Function = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\gamma_{i,exp}^{m} - \gamma_{i,calc}^{m}}{\gamma_{i,exp}^{m}}\right| + \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\rho_{i,exp}^{liq} - \rho_{i,calc}^{liq}}{\rho_{i,exp}^{liq}}\right| \qquad (33)$$

5. Optimization of parameters for electrolyte solutions in different temperature ranges

Generally, in this treatise, the parameters of the binary interaction 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.*

In this treatise, the salt-based optimization method is used, and for optimization, the Nelder-Mead (Fminsearch) method is used to adjust the parameters.

In this treatise, optimization is done based on salt. Here it is assumed that $k_{ij}=k_{ji}$ *and also the interaction parameter of two identical molecules or two ions is set equal to zero.*

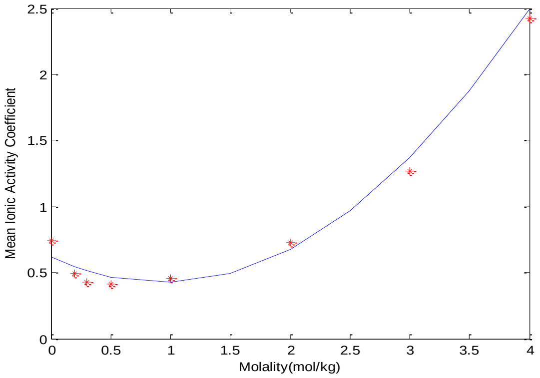

Fig 2. *Comparison of calculated and experimental average ionic activity coefficient according to the molality of* $CaCl_2$ *in the two-component system* $CaCl_2 - H_2O$ *at a temperature of 298.15 Kelvin, %ARD = 0.71, laboratory data (*) and calculation (-)*

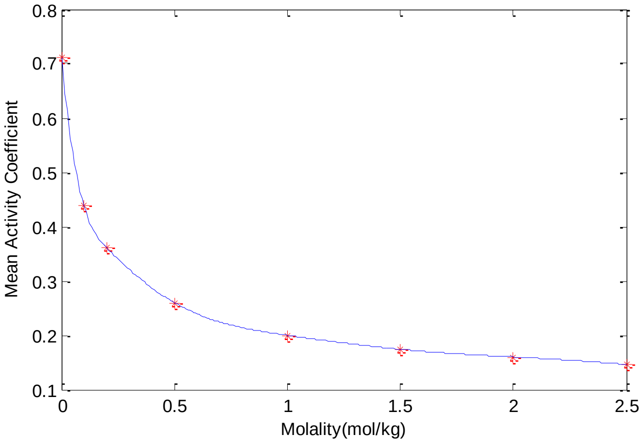

Fig 3. *Comparison of calculated and experimental average ionic activity coefficient according to the molality of* K_2SO_4 *in the two-component system* $K_2SO_4 - H_2O$ *at a temperature of 298.15 Kelvin, %ARD = 0.19, laboratory data (*) and calculations (-)*

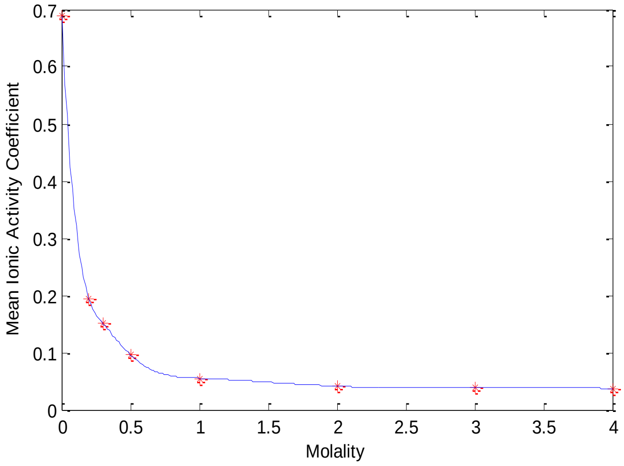

Fig 4. *Comparison of calculated and experimental average ionic activity coefficient in terms of* $CaCl_2$ *molality in the two-component system* $CaCl_2 - H_2O$ *at a temperature of 598.15 Kelvin, %ARD=1.1 , laboratory data (*) and calculation (-)*

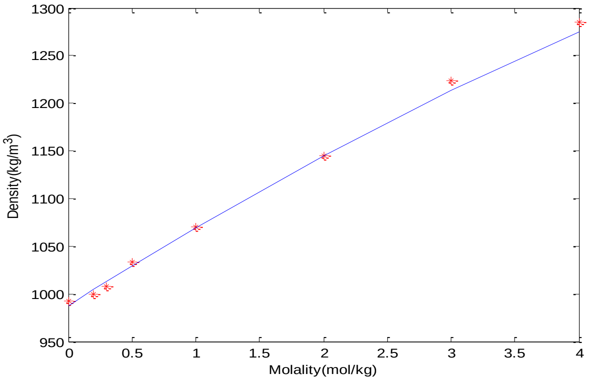

Fig 5. *Comparison of the calculated and experimental density according to the molality of* $CaCl_2$ *in the two-component system* $CaCl_2 - H_2O$ *at a temperature of 323.15 Kelvin, %ARD = 3.19, laboratory data (*) and calculation data (-)*

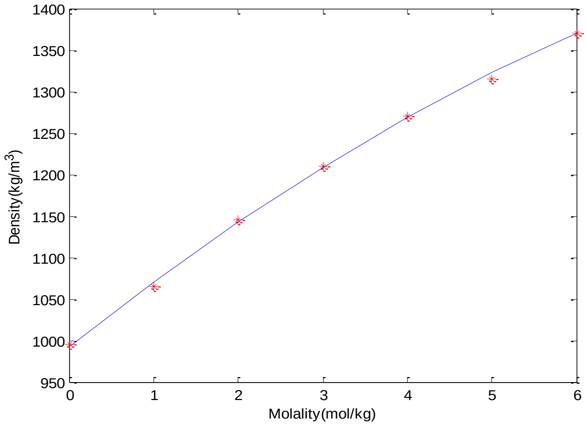

Fig 6. *Comparison of the calculated and experimental density according to the molality of NaBr in the two-component system $NaBr - H_2O$ at a temperature of 298.15 K, %ARD = 1.75, laboratory data (*) and calculation data (-)*

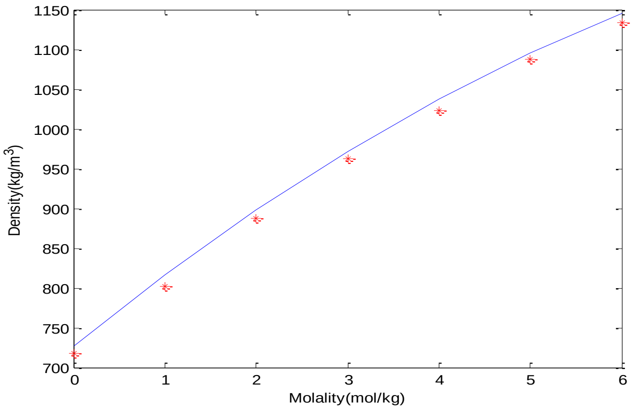

Fig 7. *Comparison of the calculated and experimental density according to the molality of NaBr in the two-component system $NaBr - H_2O$ at a temperature of 573.15 K, %ARD = 3.88, laboratory data (*) and calculation data (-)*

6. Conclusions

In this work, using Peng-Robinson equation of state and Born and MSA terms, fugacity coefficient, density are predicted for electrolyte systems. In this modeling, a large amount of experimental data has been collected for electrolyte systems. In this modeling, salt-based optimization is used, and van der Waals attraction parameter, van der Waals excluded volume parameter, ion diameter parameter, and salt-molecule binary interaction parameter are optimized by fitting the experimental data of liquid density and average ion average. Density and average ionic activity coefficients in some electrolyte solutions were predicted with high accuracy .For example the Average relative deviation for prediction of average ionic activity coefficients for calcium chloride in its solution at 298.15K and 598.15K is obtained 0.71% , 1.1% respectively; and the Average relative deviation for prediction of density for Sodium bromide solution at 313.15K and 573.15K is obtained 1.75%, 3.88% respectively.

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