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Use of Pitzer's model to calculate thermodynamic properties of aqueous electrolyte solutions of sulfuric acid

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Abstract: Over this study we calculated the coefficients of activity of different species and the concentration in the presence of H^+ ion when H_2SO_4 is alone in solution. The coefficient of average activity was calculated using the model of Pitzer. The constants of dissociation of these reactions were calculated from the values of the free standard energies. The reaction reaches a balance while producing H^+, HSO_4^- and SO_4^{2-}. The research reported here concentrated on the effect of some important operational parameters on dissolution process. The parameters were investigated and their ranges are as follows: initial molality ranging from 0.001 to 5 mol.kg^{-1} and temperatures between 25 and 200°C. Fortran 90 (Mathematical formula translating system) was used to perform all mathematical calculations. The numerical code can be used to calculate the molarity of ion H^+ of an aqueous solution of sulfuric acid. The objective of the present work is to optimize the parameters of leaching such as activity of sulfuric acid on the dissociation phenomena.

Keywords: Leaching, Pitzer, activity, dissociation, molality.

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1. INTRODUCTION

Several test were conducted to develop models to represent the thermodynamic properties of the solutions of electrolyte. The coefficient of average activity was calculated using the model of Pitzer (1-3). The pitzer ion interaction model, similar to the virial equation used for non-ideal gases, has proved to be the most accurate thermodynamic model up to moderate concentrations in aqueous solutions (4,5).

Pitzer et al. (6-8) developed a model for calculation of the properties of the electrolytes starting from a semi numerical models and an improved analysis of the model of DEBYE HUCKEL.

This model links the intermolecular forces and the distribution of the ions to the osmotic pressure and takes into account the influence of forces with short distance in the binary interactions. The expressions of the coefficient of activity and the osmotic coefficient are deduced from the equation of the excess free energy of GIBBS. The obtained equations are analogous to those of GUGGENHEIM.

Pitzer's model is capable of precisely forecasting activity and enthalpy provided that the variation of the parameters with temperature are recognized. This variation has been calculated for some electrolytes (9-11).

Zomaitis et al. suggested to admit the parameters to be constant and to consider the influence of temperature only on the DEBYE-HUCKEL (12).

The mixing terms for ions with same sign but with unequal magnitude are not included in the Pitzer ion interaction, Harvie et al. have found these terms (13).

Archer discovered that an ion strength reliant third virial parameter describing the combined interactions between two similar cations and anion or vice versa (14).

Pitzer et al. introduced a Margules type equation to model aqueous solutions up to a pure salt (15).

Sippola found out that only four parameters with a simple temperature dependency in enough to present the osmotic and activity coefficients (16).

Knopf et al. were found to be extrapolate the measured osmotic coefficient within a maximum deviation of 0.01 (17).

The aim of our work was to optimize leaching parameters such as the activity of sulfuric acid. We developed from fortran 90 a program, for simulating this process and predicting its performance.This numerical code is based on the mathematical description of the detailed physical and chemical phenomena occurring.

2. METHODS

2.1. Thermodynamic Model

The Pitzer thermodynamics model is used extensively to describe the interactions between dissolved ions and solvents (18).

In water, Sulfuric acid is separated according balances (19-22).

$$H_2SO_4 \Leftrightarrow H^+ + HSO_4^- \qquad \mathrm{K}_1$$
$$HSO_4^- \Leftrightarrow H^+ + SO_4^{-2} \qquad \mathrm{K}_2$$

The dissociation constants of these reactions are calculated from the values of the standard free energy of species considered.

The equilibrium constant is linked to the standard free energy of the reaction by the relation VAN'T HOFF:

$$\frac{\Delta G^0}{T} = -RTLnK$$

he just:

$$K_1 = e^{\left(-\frac{\Delta G^0_{HSO_4^-} - \Delta G^0_{H_2SO_4}}{RT}\right)} = 80.72$$

$$K_2 = e^{\left(-\frac{\Delta G^0_{SO_4^{-2}} - \Delta G^0_{HSO_4^-}}{RT}\right)} = 0.0125$$

K: equilibrium constant
ΔG^0 : standard free energy
T: Temperature (K)
R: Gas constant $\mathrm{Jmol^{-1}K^{-1}}$

The high values of the equilibrium constant K_1, translated into strong shift in the balance towards the formation of HSO_4^- and H^+. We admit that in the future the first dissociation H_2SO_4 is total. Only the second equilibrium dissociation will be taken into account ($HSO_4^- \Leftrightarrow H^+ + SO_4^{2-}$).

Pitzer et al. gives value perceptibly different k_2. It adopts the value 0.0105, which corresponds to a compromise (6).

An application of Pitzer 's expression for estimating the coefficient of activity for a mixture of electrolytes to the couple of ions H^+ and SO_4^{-2} in the presence of ions HSO_4^- gives:

$$ln(\gamma_{H_2SO_4}) = 2f^{\gamma} + \frac{4}{3}m_1B_{H_1} + \frac{1}{3}(4m_2 + 2m_H)B_{H_2}^{(0)} + \frac{1}{3}(8m_2 + 2m_H)m_HC_{H_2} + 2m_1m_HB'_{H_1}$$

γ_i: Activity coefficient of a component i
f^{γ}:the derivative of the Debye-Huckel term
m_i: Molale concentration of component i
B_{ij}: Pitzer binary interaction parameters
C_{ij}: Pitzer ternary interaction parameter
HSO_4^- is indexed by 1
SO_4^{-2} is indexed by 2

Because the molecule H_2SO_4 was supposed to be made of two ions H^+ and SO_4^{-2}, then we have:

$$ln\,\gamma_{H_2SO_4} = \frac{1}{3}(2\,ln\,\gamma_H + ln\,\gamma_{SO_4}),$$

Hence; $$3\,ln\,\gamma_{H_2SO_4} = ln(\gamma_{H^+}^2\gamma_{SO_4})$$

The computed exploratory Pitzer showed that $B_{H_2}^{(1)}$ had a negligible effect on the determination of the activity coefficient, expressing β_{H_2} in those circumstances is tantamount to match. β_{H_2} and $B_{H_2}^{(0)}$. On the other hand, good results are obtained either with the combination $B_{H_2}^{(0)}$ and C_{H_2}, or combination C_{H_1} and C_{H_2}, but the first was raised slightly better and has been adopted. It follows $C_{H_1} = 0$.

The term B'_{H_2} is void because it represents the derivative compared to the ionic strength of a term $B_{H_2}^{(0)}$ independent I.

This method ensures the relation:

$$ln(\gamma_H^2\gamma_{SO_4}) = 6f^{\gamma} + 4m_1B_{H_1} + (4m_2 + 2m_H)B_{H_2}^{(0)} + (8m_2 + 2m_H)m_HC_{H_2} + 6m_1m_HB'_{H_1}$$

Now let us apply the expression of the coefficient of activity for a mixture of electrolytes to the couple of ions H^+, HSO_4^- in the presence of ions SO_4^{-2}.

The species H_2SO_4 being supposed constitute of the ions H^+ and HSO_4^-, one thus has:

$$ln\,\gamma_{H_2SO_4} = \frac{1}{2}ln\,\gamma_H\,ln\,\gamma_{HSO_4^-}$$

with; $$ln\,\gamma_H\,ln\,\gamma_{HSO_4} = 2f^{\gamma} + 2(m_1 + m_H)B_{H_1} + 2m_2B_{H_2}^{(0)} + 4m_2m_HC_{h_2} + 2m_1m_HB'_{H_1}$$

The former relationships must be compatible with the balance of dissolution. Hence the expression of the product of the coefficients of activity is as follows:

$$ln(\gamma_{H^+}^2\gamma_{SO_4^-} - ln\,\gamma_{H^+}\,\gamma_{HSO_4^-} = ln(\frac{\gamma_{H^+}\gamma_{SO_4^-}}{\gamma_{HSO_4^-}}) = 4f^{\gamma} + 2(m_1 - m_H)B_{H_1} + 2(m_2 + m_H)B_{H_2}^{(0)} + 2(2m_2 + m_H)B_{H_2}^{(0)} + 2(2m_2 + m_H)m_HC_{H_2} + 4m_1m_HB'_H$$

where:

$$\frac{\gamma_{H^+}\gamma_{SO_4^-}}{\gamma_{HSO_4^-}} = exp(\,4f^{\gamma} + 2(m_1 - m_H)B_{H_1} + 2(m_2 + m_H)B_{H_2}^{(0)} + 2(2m_2 + m_H)B_{H_2}^{(0)} + 2(2m_2 + m_H)m_HC_{H_2} + 4m_1m_HB'_H)$$

At weak concentrations, the molality is close to the concentration on the basis of the second balance of the dissolution of the H_2SO_4.

The concentration of the sulfate ions in the solution makes it possible to write the following relationship:

$m = m_1 + m_2$ therefore $m_2 = m - m_1$

According to Pitzer we have:

$$m = \frac{1000C}{1000\rho - MC}$$

m: Molality
C: concentration
M: Molar mass
ρ: Density

On the other hand, because of the electric neutrality of the solution $m_H = m_1 + 2m_2$

From where $m_1 = 2m - m_H$

The constant of equilibrium of dissociation of the H_2SO_4 is then:

$$k_2 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \bullet \frac{\gamma_H\gamma_{SO_4}}{\gamma_{HSO_4}} = \frac{m_Hm_2}{m_1} \bullet \frac{\gamma_H\gamma_2}{\gamma_1}$$

with; $$m_H = \frac{\frac{K_2m_1}{m_2}}{(\frac{\gamma_H\gamma_2}{\gamma_1})}$$

An average coefficient of activity $\gamma^{\pm}$ can be defined by assuming that the H_2SO_4 is completely dissociated. The following relationship: $4\gamma_{\pm}^3m^3 = \gamma_H^2\gamma_{SO_4}m_H^2m_2$ allows to calculate the average coefficient of activity $\gamma_{\pm}$.

Indeed, the molality of ions H^+ was determined and one calculates $(\gamma_H^2\gamma_{SO_4})$ as follows:

$$ln(\gamma_H^2\gamma_{SO_4}) = 6F^{\gamma} + 4m_1B_{H_1} + (4m_2 + 2m_H)B_{H_2}^{(0)} + (8m_2 + 2m_H)m_HC_{H_2} + 6m_1m_HB'_{H_1}$$

with; $C_{H_2} = \frac{C^{\gamma}_{H_2}}{2^{\frac{3}{2}}}$

$$f^{\gamma} = A^{\gamma}(\frac{I^{\frac{1}{2}}}{1+1.2I^{\frac{1}{2}}} + \frac{2}{1.2} ln(1+1.2I^{\frac{1}{2}}))$$

$$A^{\gamma} = 0.0000043T^2 + 0.002709T + 0.583022$$

I: ionic strength
A^{γ}: DEBYE-HÜCKEL parameter
T: Temperature (K)
The temperature T is given in Kelvin

$$B_{H1} = B^{(0)}_{H1} + \frac{B^{(1)}_{H1}}{2I}(1-(1+2I^{\frac{1}{2}})e^{(-2I^{\frac{1}{2}})})$$

$$B'_{H1} = \frac{B^{(1)}_{H1}}{2I^2}(1-(1+2I^{\frac{1}{2}}+2I)e^{(-2I^{\frac{1}{2}})})$$

$$C_{H_2} = \frac{C^{\gamma}_{H_2}}{2^{\frac{3}{2}}}$$

For an aqueous sulfuric solution, the ionic species involved are: H^+, HSO_4^- and SO_4^{2-}.

Therefore; $I = \frac{1}{2}m_H + \frac{1}{2}m_1 + \frac{1}{2}m_2 2^2$

Pitzer provides the following equations, depending on the temperature (8):

$$k_2 = e^{-14.0321+\frac{2825.2}{T}}$$

$$B^{(0)}_{H1} = 0.05584 + \frac{46.040}{T}$$

$$B^{(1)}_{H_1} = -0.65758 + \frac{336.514}{T}$$

$$B^{(0)}_{H_2} = -0.32806 + \frac{98.607}{T}$$

$$C_{H_2} = 0.25333 - \frac{63.124}{T}$$

2.2. Optimization of Model Parameters

The model of Pitzer was applied to calculate the average coefficients of activity and the molality in ion H+ of an aqueous solution of sulfuric acid. To this purpose, the numerical code for solving equations is written (in FORTRAN 90). The program can be used to calculate the molality of ion H^+ of an aqueous solution of H_2SO_4 of an initial molality ranging from 0.001 to 5 mol.kg^{-1} at temperatures between 25 and 200°C.

3. RESULTS

The term $ln\frac{\gamma_H\gamma_2}{\gamma_1}$ involved in the expression of the constant of dissolution depends on the molality mH of ion H^+. An iterative calculation is done by fixing an initial molality mH superior than the initial molality in sulfuric acid. The following equations allow the calculation of a new value of the molality. A comparison test between the previous and newly calculated value refining the result with an accuracy of 10^{-5} mol.kg^{-1}.

m_1=2m-m_H,
m_2=m-m_1

and;

$$m_H = \frac{\frac{K_2 m_1}{m_2}}{(\frac{\gamma_H\gamma_2}{\gamma_1})}$$

Figure 1 gives the molality in ions H^+ for different temperatures with molalities in H_2SO_4 lying between 0.01 and 0.25 mol kg^{-1}.

Figure 2 provides the molality in ions H^+ for different temperature with molalities in H_2SO_4 from 0.5 to 5 mol.kg^{-1}.

For molality higher than 1 mol.kg^{-1} and temperatures within 170-200°C, the molality in ion H^+ passes by a minimum.

Figure 3 shows the molality of H^+ as a function of the molarity of H_2SO_4 dependence shows between the two molalities whatever the temperature.

It can be noted that the temperature does not any influence on the calculated molality in ion H^+ as a function of the molality in H_2SO_4 at 25°C.

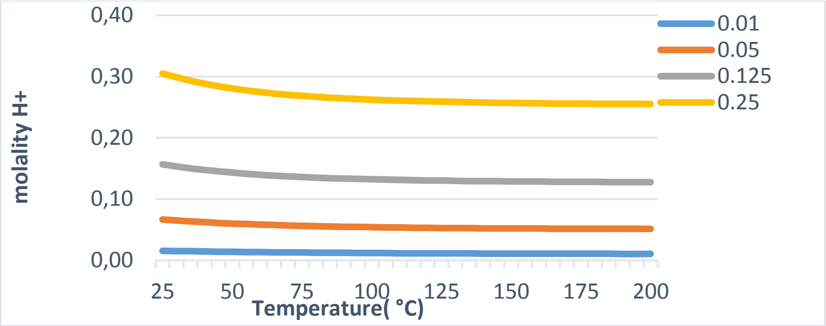

Figure 1: Molality in H$^+$ versus the temperature for sulfuric aqueous solutions from 0.01 to 0.25 mol kg^{-1}.

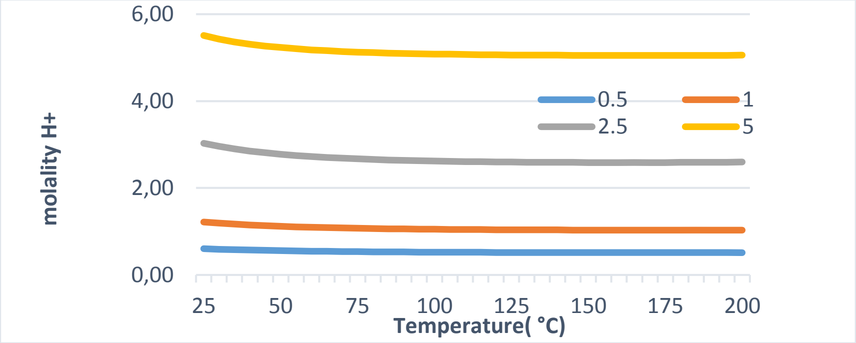

Figure 2: Variation in molality of H$^+$ as a function of the temperature for sulfuric aqueous solutions in the range of 0.5 to 5 mol.kg^{-1}.

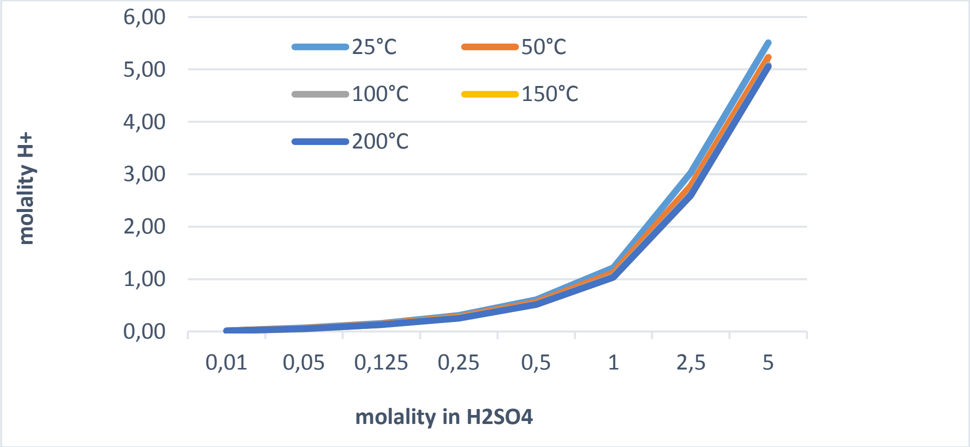

Figure 3: Variation in molality of H$^+$ versus of that of sulfuric acid at various temperatures.

Let m be the stochiometric concentration in sulfuric acid, and m_H the concentration in ion H$^+$ in equilibrium.

The expression giving the balance of the sulfate ions can be written as:

$$m_H{}^3 + k_1 m_H{}^2 + (k_1 k_2 - m k_1) m_H - 2 k_1 k_2 = 0$$

The solving of this cubic equation in m_H gives a concentration in ion H$^+$ at equilibrium for 25 °C approximately with a concentration of ions H$^+$ equals to 0.135M. The stochiometric concentration m being equal to 0.125M.

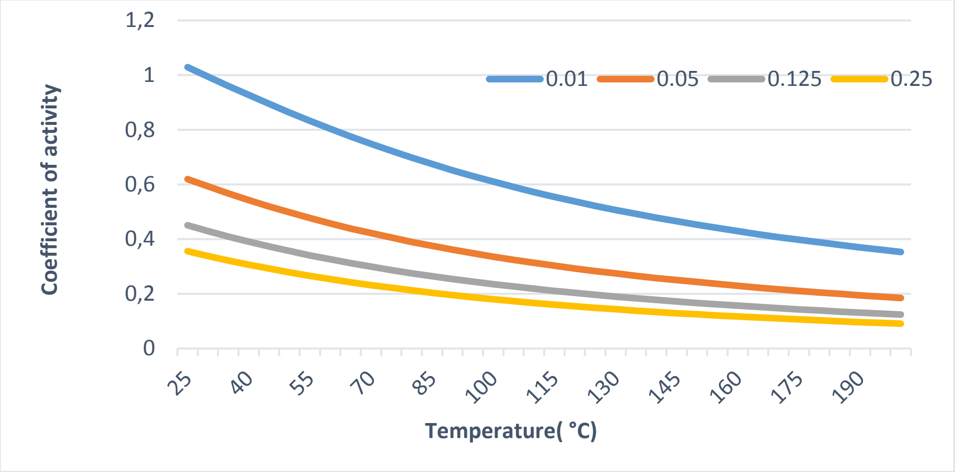

Figure 4: Evolution of the activity coefficient of the H_2SO_4 as a function of the temperature between 0.01 and 0.25.

The comparison with the value extracted from Figure.1 for the same stochiometric concentration gives a value of the concentration in ion H^+ equal to 0.1566519M i.e. a difference of 16.038% compared to the value of this same concentration obtained without taking into account the activities.

Figure 4 gives the values of the activity coefficient of the H_2SO_4 in dependence of the temperature for the molalities ranging from 0.01 to 0.25 mol.kg$^{-1.}$ Whatever the molality, the coefficient of activity $\gamma_{\pm}$ for the H_2SO_4 decreases when the temperature increases.

4. CONCLUSION

In the temperature range considered: 25 to 200°C, this study allows the determination of concentration in ion H^+ and the coefficients of activity of different kinds of the H_2SO_4 alone in solution. In an aqueous solution of H_2SO_4, the species reacting are H^+, HSO_4^- and SO_4^{2-}. We can consider that the H_2SO_4 with the two kinds of anions HSO_4^- and SO_4^{2-} and the cations H^+, constitute a mixed electrolyte for the equation of Pitzer.

The solving of the expression giving the balance of the sulfate ions gives a concentration in ion H^+ at equilibrium for 25 °C approximately with a concentration of ions H^+ equals to 0.135M. The stochiometric concentration m being equal to 0.125M. The comparison with the value extracted from figure for the same stochiometric concentration gives a value of the concentration in ion H^+ equal to 0.1566519M i.e., a difference of 16.038% compared to the value of this same concentration obtained without taking into account the activities.

It can be noted that the temperature does not any influence on the calculated molality in ion H^+ as a function of the molality in H_2SO_4 at 25°C.

For molality higher than 1 mol.kg^{-1} and temperatures within 170-200°C, the molality in ion H^+ passes by a minimum.

The coefficient of activity $\gamma_{\pm}$ for the H_2SO_4 decreases when the temperature increases.

The calculation results are in good agreement with those found in literature.

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