Physicochem. Probl. Miner. Process., 59(5), 2023, 167497

Physicochemical Problems of Mineral Processing

http://www.journalssystem.com/ppmp

ISSN 1643-1049

The influence of activity coefficient and equilibrium constant models on the speciation of aqueous solutions of H_2SO_4–$MgSO_4$–$Al_2(SO_4)_3$ at 235 and 250 °C

Okechukwu Vincent Dickson [1,3], Thomas Deleau [1], Christophe Coquelet [1,2], Fabienne Espitalier [1,2], Julien Lombart [3], Antoine Tardy [3]

[1] University of Toulouse, IMT Mines Albi, UMR CNRS 5302, RAPSODEE Centre, Campus Jarlard, Albi Cedex 09 F-81013, France

[2] Mines Paris, PSL University, CTP Centre Thermodynamique des Procédés, 35 rue Saint Honoré 77305 Fontainebleau Cedex, France

[3] Prony Resources New Caledonia, Usine du grand sud, route de Kwa neie – Prony – Bp 218, New – Caledonia

Corresponding author: christophe.coquelet@mines-albi.fr

Abstract: Supersaturation occurs in many industrial applications promoting reactive crystallisation between the reactants to form solutes. These solutes accumulate during precipitation, leading to the formation of scales on the inner walls of the reactor and particularly around the stirrer, causing modifications in the hydrodynamics. This encrustation is responsible for process shutdowns in continuous crystallisation processes. Supersaturation control is essential for industrial processes aimed at controlling or inhibiting the formation of these solids. Knowledge of mineral solubility and chemical speciation is required to account for the composition of the complexes in the system in their various solid or aqueous forms. This speciation is obtained by considering the thermodynamic equilibrium constants of the dissociation/complexation reactions involved in the system, the pressure, and the activity coefficients of the chemical species in their molecular or electrolyte form. From these thermodynamic quantities and the state of the system, we can predict the direction of the reaction. This study highlights the risk of the lack of experimental information on equilibrium constants at high temperatures and moderate pressures. Our goal is to evaluate the accuracy of existing models classically used to predict the equilibrium constant in such very hard conditions encountered in hydrometallurgical processes. Furthermore, we demonstrate the influences of equilibrium constants estimation and activity coefficient models on the speciation of H_2SO_4–$Al_2(SO_4)_3$–$MgSO_4$ systems, forming hydronium alunite and kieserite in the laterite liquor of hydrometallurgical processes.

Keywords: activity coefficient, equilibrium constant, hydrometallurgy, speciation, thermodynamics

1. Introduction

Speciation calculations allow the chemical composition of species in solution to be determined at specific conditions. Direct speciation measurements are complex and require specific techniques depending on the studied metal (Yan & Ni, 2001; Moldovan et al., 2004).

The High-Pressure Acid Leaching (HPAL) mechanism consists of the dissolution of the desired metals (Ni, Co, etc.) from the mineral matrix with strong acid, followed by the hydrolysis and precipitation of insoluble oxides and sulphates of iron, aluminium, and silica. In hydrometallurgy which utilises high temperatures and pressures in the range of 230–270 °C (Whittington & Muir, 2000) and 30–56 bar (Gultom & Sianipar, 2020), respectively, metals are separated based on their difference in solubilities and other electrochemical properties (Meshram et al., 2019).

Optimal leaching conditions vary according to the mineralogy of the ore being processed (Whittington & Muir, 2000). During the hydrometallurgical treatment process, complex formation and electrolyte dissociation occur simultaneously in the aqueous solutions formed. In a typical solute and

DOI: 10.37190/ppmp/167497

solvent mixture, ions in the solution interact with each other. At low salt concentrations, these interactions are small and negligible due to their low impacts. But, they chemically behave like they are less concentrated than they are in reality at higher concentrations. However, other insoluble or poorly soluble complexes may precipitate. The activity coefficient accounts for the sample's deviation from the ideal mixing behaviour in a mixture of chemical substances. Modelling the speciation of electrolytes in solution is an indispensable tool for the development, analysis, and control of supersaturation (Papangelakis et al., 2004). The objective of this paper is to select the best model (activity coefficient & equilibrium constant) combination, considering the unavailability of experimental data in the operating conditions of HPAL. As a case study to realize this selection, we have considered the study of Baghalha & Papangelakis, (1998) and Marshall & Slusher (1965) where the measured experimental data in our domain of temperature and pressure of interest are available.

1.1 Activity coefficients models $(\gamma_{i,T})$

The activity coefficient measures the deviation from the ideal mixture and can be calculated from various models (Bromley, 1973; Helgeson & Kirkham, 1974; Zemaitis et al., 1986; Pitzer, 1991). These models differ in their degree of complexity (Helgeson, 1981; Ross, 2012) and are computed as a function of ionic strength and temperature. Due to the intricacy of the Pitzer activity coefficient model, Eqs. (1), (2), and (3+4) were used in our investigations to compare the influence of these activity coefficient models on aqueous solution speciation with values obtained from the Pitzer model and experimental data.

Truesdell-Jones (Extended Debye-Hückel)

$$\log\left(\gamma_{i(T)}\right) = -\frac{Z_j^2\, A_\gamma \sqrt{I}}{1+\acute{\alpha} B_\gamma \sqrt{I}} + b_b I \tag{1}$$

Davies

$$\log\left(\gamma_{i(T)}\right) = -Z_j^2\, A_\gamma \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \tag{2}$$

Bromley

$$\log\left(\gamma_{i(T)}\right) = \frac{-|Z_+Z_-|_j\, A_\gamma \sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.6B)|Z_+Z_-|_j I}{\left(1+\frac{1.5I}{|Z_+Z_-|_j}\right)^2} + BI \tag{3}$$

Meissner

$$\log\left(\gamma_{i(T)}\right) = |Z_+Z_-|_j \left((1.125 - 0.005T)\log\left(\gamma_{i(25^oC)}{}^{\frac{1}{|Z_+Z_-|_j}}\right) - (0.125 - 0.005T)\left(-\frac{0.41\sqrt{I}}{1+\sqrt{I}} + 0.039I^{0.92}\right)\right) \tag{4}$$

In Eqs. (1)–(4), I is the ionic strength expressed as $I = 0.5(\sum m_j \times Z_j^2)$, where m_j is the molality of ionic species j, and Z_j is the charge of ionic species (squared), which can also be represented as $|Z{+}Z{-}|_j$ as seen in Eqs. (3) and (4) if the computation involves a molecular species. $\gamma i(T)$ is the mean molar activity coefficient at a given temperature. $A\gamma$ ($kg^{0.5}mole^{-0.5}$) and/or $B\gamma$ ($kg^{0.5}mole^{-0.5}cm^{-1}$) in Eqs. (1) – (3) are the Debye-Hückel parameters (Helgeson & Kirkham, 1974). bb (kg/mol) and $\acute{\alpha}$ (cm) in Eq. (1) are the experimentally determined parameters for ionic species (Parkhurst, 1990; Langmuir, 1997). B (kg/mol) in Eq. (3) is an interaction parameter between ions, its value for some salt species is reported by Bromley, (1973) at 25 °C. T (°C) in Eq. (4) is the temperature of interest (Zemaitis et al., 1986).

1.2 Equilibrium constant models $(K_{i,T})$

The equilibrium constant of a given chemical reaction is the value of its reaction quotient at chemical equilibrium. It is affected by reaction parameters such as temperature, solvent, and ionic strength. Knowledge of the equilibrium constant is essential to understanding many chemical systems. Unlike a change in pressure or concentration of the reactants, temperature changes result in changes in the value of the equilibrium constant. The calculation of the equilibrium constant at reference conditions (298.15 K and 1 bar) is easy, provided that values for the standard thermodynamic properties are available. However, extrapolation at a higher temperature is not straightforward. Different models for the computation of the equilibrium constants at temperatures other than 25 °C have been developed by different authors (Hoff, 1896; Helgeson, 1967; Cobble et al., 1982; Anderson et al., 1991). The Density model, which gives similar values to the Revised HKF model (Liu & Papangelakis, 2005) has been ascertained to be the "best" owing to its simplicity and assumption (Anderson et al., 1991). The models in Eqs. (5) – (8) were used for modelling the equilibrium constants of aqueous species in this study.

a. The Unexpanded Helgeson-Kirkham-Flowers (HKF) model

$$\log\left(\mathrm{K_{i,T}}\right) = \frac{\Delta \mathrm{S}^{\circ}_{\mathrm{i,\,25^{o}}C}}{2.303\mathrm{RT}}\left(298.15 - \frac{219}{\mathrm{w}}\left(1 - \exp\left(\exp(\mathrm{b} + \mathrm{aT}) - \mathrm{c} + \frac{\mathrm{T} - 298.15}{\theta}\right)\right)\right) - \frac{\Delta \mathrm{H}^{\circ}_{\mathrm{i,\,25^{o}}C}}{2.303\mathrm{RT}} \quad (5)$$

where $a = 0.01875,\ b = -12.741,\ c = 0.000784,\ w = 1.003229$

Eq. (5) is applied only where the enthalpy and entropy of dissociation at 25 °C are both negative. This is also true for certain reactions for which enthalpy is a large positive number and the entropy is negative (Helgeson, 1967).

b. The Density model

$$\ln\left(\mathrm{K_{i,T}}\right) = \ln\left(\mathrm{K_{i,\,25^{o}}}_C\right) - \frac{\Delta \mathrm{H}^{\circ}_{\mathrm{i,\,25^{o}}C}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}} - \frac{1}{298.15}\right) + \frac{\Delta \mathrm{Cp}^{\circ}_{\mathrm{i,\,25^{o}}C}}{298.15\mathrm{R}\left(\frac{\partial \alpha}{\partial \mathrm{T}}\right)_{\mathrm{P^{\circ}=1\ bar}}}\left(\frac{1}{\mathrm{T}}\ln\left(\frac{\rho_{(25^{o}C,1\mathrm{bar})}}{\rho}\right) - \frac{\alpha_{25^{o}C}}{\mathrm{T}}(\mathrm{T} - 298.15)\right) \quad (6)$$

α is the coefficient of thermal expansion of H_2O. $\rho_{(25^{o}C,1\mathrm{bar})}$ and ρ is the density of the medium (water) at the reference temperature and the desired temperature respectively (Helgeson & Kirkham, 1974; Anderson et al., 1991).

c. The van't Hoff model

$$\ln\left(\mathrm{K_{i,T}}\right) = \ln\left(\mathrm{K_{i,\,25^{o}}}_C\right) - \frac{\Delta \mathrm{H}^{\circ}_{\mathrm{i,\,25^{o}}C}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}} - \frac{1}{298.15}\right) \quad (7)$$

d. Determination from regressed experimental data correlation

$$\log\left(\mathrm{K_{i,T}}\right) = \mathrm{A} + \mathrm{BT} + \mathrm{CT}^{-1} + \mathrm{Dlog(T)} + \mathrm{ET}^{-2} \quad (8)$$

where T is the temperature (K) and $\mathrm{Log}\left(\mathrm{K_{i,T}}\right) \equiv \log_{10}\left(\mathrm{K_{i,T}}\right) \equiv \frac{\ln(\mathrm{K})}{\ln(10)}$.The parameters R, $\Delta \mathrm{S}^{\circ}_{\mathrm{i,\,25^{o}C}}$, $\Delta \mathrm{H}^{\circ}_{\mathrm{i,\,25^{o}C}}$, $\Delta \mathrm{Cp}^{\circ}_{\mathrm{i,\,25^{o}C}}$ in Eqs. (5) – (7) are the gas constant (8.314 $\mathrm{JK^{-1}mol^{-1}}$), entropy, enthalpy and the specific heat capacity of the reaction. A, B, C, D and E in Eq. (8) are parameters determined by experimental fitting from the Thermoddem database.

2. Methodology and calculation

a. Equilibrium constant determination

To confirm the influence of different thermodynamic equilibrium constant models on the obtained equilibrium constant results, four dissociations (two for aluminium species and two for magnesium species) reactions were considered.

$$\mathrm{AlSO_4^+} \leftrightharpoons \mathrm{Al^{3+}} + \mathrm{SO_4^{2-}} \quad (\mathrm{I})$$

$$\mathrm{Al(SO_4)_2^-} \leftrightharpoons \mathrm{Al^{3+}} + 2\mathrm{SO_4^{2-}} \quad (\mathrm{II})$$

$$\mathrm{MgSO^{o}_{4(aq)}} \leftrightharpoons \mathrm{Mg^{2+}} + \mathrm{SO_4^{2-}} \quad \mathrm{III)}$$

$$\mathrm{MgSO_4{\cdot}H_2O_{(s)}} \leftrightharpoons \mathrm{Mg^{2+}} + \mathrm{SO_4^{2-}} + \mathrm{H_2O} \quad (\mathrm{IV})$$

b. Speciation

For the speciation of the solid formation, predominant reactions leading to the formation of Hydronium-alunite and Kieserite as specified by Baghalha & Papangelakis, (1998) were considered for the aluminium species and magnesium species respectively.

$$\mathrm{H_2O} \leftrightharpoons \mathrm{H^+} + \mathrm{OH^-} \quad (\mathrm{V})$$

$$\mathrm{HSO_4^-} \leftrightharpoons \mathrm{H^+} + \mathrm{SO_4^{2-}} \quad (\mathrm{VI})$$

Aluminium species (H-alunite formation)

$$\mathrm{Al^{3+}} + \mathrm{SO_4^{2-}} \leftrightharpoons \mathrm{AlSO_4^+} \quad (\mathrm{XI})$$

$$2\mathrm{AlSO_4^+} + \mathrm{HSO_4^-} \leftrightharpoons \mathrm{Al_2(SO_4)^{o}_{3(aq)}} + \mathrm{H^+} \quad (\mathrm{VIII})$$

$$3\mathrm{AlSO_4^+} + 7\mathrm{H_2O} \leftrightharpoons \mathrm{(H_3O)Al_3(SO_4)_2(OH)_{6(s)}} + 4\mathrm{H^+} + \mathrm{HSO_4^-} \quad (\mathrm{IX})$$

Magnesium species (Kieserite formation)

$$Mg^{2+} + SO_4^{2-} \leftrightarrows MgSO^o_{4(aq)} \tag{X}$$

$$MgSO^o_{4(aq)} + H_2O \leftrightarrows MgSO_4{\cdot}H_2O_{(s)} \tag{XI}$$

Rxns. (V), and (VI) were used in both cases for both solid speciations. For Aluminium species, the values of the equilibrium constant $K_{(VI)}$, and $K_{(VII)}$ were computed from the respective equilibrium constant models in Eqs. (5) – (8). On the other hand, the values of $K_{(V)}$ (Marshall & Franck, 1981), $K_{(VIII)}$ and $K_{(IX)}$ as reported by Baghalha & Papangelakis, (1998) were maintained due to the unavailability of the complete thermodynamic data ($\Delta H^{\circ}_{f,25\,^oC}, S^{\circ}_{25\,^oC}, \overline{Cp}^{\circ}_{25\,^oC}$) of the species needed for the computation with our various models. While for magnesium species, the equilibrium constants value $K_{(V)}$, $K_{(VI)}$, $K_{(X)}$, and, $K_{(XI)}$, for the four reactions were computed from the respective equilibrium constant models [Eqs. (5) – (7)] used for the extrapolation.

For $MgSO_4$ speciation, the results obtained with the van't Hoff model were out of range, thus, the model was not considered in the Fig.. Consequently, due to the unavailability of the thermodynamic data for some species needed to compute the equilibrium constant values of the reactions used in the speciation of kieserite formation, Eq. (8) was not used for $MgSO_4$ speciation.

In the first case of the speciation for both $MgSO_4$ and $Al_2(SO_4)_3$, only the equilibrium constant models were used without taking into account the activity coefficients models. In the second case, the activity coefficient and equilibrium constant models were interchanged independently. The activity coefficient model in Eq. (4) was used to complement Eq. (3) to account for higher temperature extrapolation due to the unavailability of the "B" parameters in Eq. (3) at elevated temperatures. Thus, Eqs. (3), and (4) were combined as one model for the 'Bromley + Meissner' activity coefficient ($\boldsymbol{\gamma}_i$) calculation.

The MATLAB software was used to resolve the equations and the solubility results compared with the experimental data of H_2SO_4–$Al_2(SO_4)_3$ (Baghalha, 1999), H_2SO_4–$MgSO_4$ (Marshall & Slusher, 1965) and the calculated values from Baghalha & Papangelakis, (1998) obtained with the Pitzer activity coefficient model and fitted equilibrium constant values. The values of the calculated equilibrium constant for each participating species in Rxns. (V) – (XI) using Eqs. (5) – (8) and the parameters for the activity coefficient models in Eqs. (1), and (3) are shown in the Appendix.

3. Results and discussion

3.1 Effects of models on the equilibrium constant values

The reference thermodynamic data (enthalpy, entropy, and specific heat capacity) of aluminium and magnesium species from Liu & Papangelakis, (2005) which is consistent with the data from Shock & Helgeson, (1988) were used for the extrapolation of the equilibrium constant values at elevated temperatures with Eqs. (5) – (7) for each participating reaction species in Rxns. (V) – (XI) within the range of 25 – 300 °C, except for Eq. (8) which is obtained from regressed experimental parameters (See Thermoddem database), hence, does not require the input of the thermodynamic data for equilibrium constant extrapolation.

Figs. 1, and 2 show the results obtained with the four equilibrium constant models in Eqs. (5) – (8) differ from one another and the deviation increases with temperature. This supports the need to choose a reliable model for the calculation of the equilibrium constants at elevated temperatures. Using different models for extrapolation gives inconsistent results, therefore, models should be validated against experimental measurements before they can be considered reliable (Liu & Papangelakis, 2005). Due to the lack of experimental data for the considered reactions [Rxns. (I) – (IV)], the results obtained from Eq. (8) were used as a base for the comparison of the models. For $MgSO_4$, $MgSO_4{\cdot}H_2O$, and $AlSO_4^+$ species, the Density equilibrium constant model gave the 'best' result with close approximation to the results calculated from the regressed experimental data across the temperature axis with a maximum deviation of 9, 10, and 10% respectively at the highest considered temperature (300 °C) in comparison with the van't Hoff and unexpanded HKF models with deviations of 40, 44, & 68% and 3, 25, & 41% respectively for the three species. For $Al(SO_4)_2^-$, the $\overline{Cp}^{\circ}_{25\,^oC}$ data were not reported, hence the reaction could not be obtained with the Density model. Likewise, the experimental fitting parameters in Eq. (8) were not documented for the species in the Thermoddem database. Hence, no comparison was made

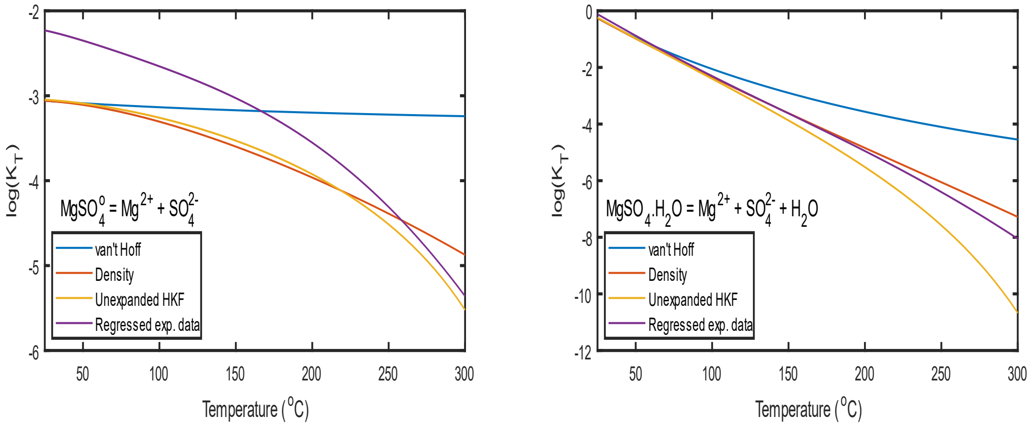

Fig. 1. Variations of equilibrium constant models for $MgSO_{4(aq)}^{o}$ (left) and $MgSO_4.H_2O_{(s)}$ (right) dissociation reaction species. The term 'Regressed exp. data' is obtained from Eq. (8).

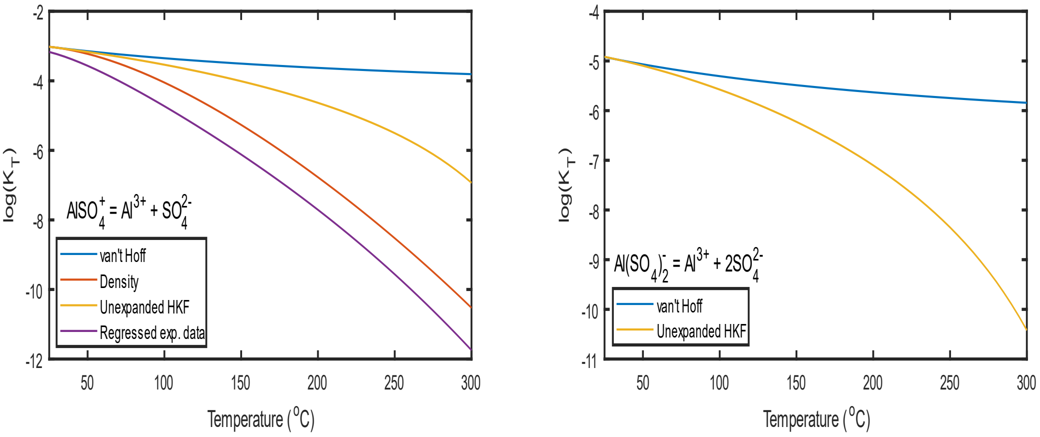

Fig. 2. Variations of equilibrium constant models for $AlSO_{4\,(aq)}^{+}$ (left) and $Al(SO_4)_{2\,(aq)}^{-}$ (right) dissociation reaction species. The term 'Regressed exp. data' is obtained from Eq. (8).

with the regressed experimental data and the Density models for $Al(SO_4)_2^-$ species. But the differences in the results obtained from the van't Hoff and unexpanded HKF models are clearly defined. The van't Hoff model is seen to have the highest deviation from other equilibrium constant models as temperatures increased above 100 °C. The model though simple to use, is not well suited for aqueous speciation, at higher temperatures. Its assumption that takes $\Delta C_{p_{i,\,25^oC}}^{\circ} = 0$ is too strong for the dissociation of most complexes and leads to errors when used to determine the equilibrium constant of a reaction (Helgeson, 1967). Figs. 1 – 2 confirm the inconsistency that arises when different models are used for the extrapolation of the equilibrium constant. The validity of these models with available experimental data is tested in Figs. 4 – 5.

3.2 Influence of activity coefficient and equilibrium constant models on speciation

In Fig. 3 with no incorporation of the activity coefficient of the reactions, there is a greater deviation in the solubility speciation values obtained from different equilibrium constant models from the experimental data compared to the results obtained in Figs. 4, and 5 which incorporate the activity coefficient models. For $Al_2(SO4)_3$ speciation in Fig. 3, the percentage deviation for the van't Hoff, unexpanded HKF, Density and Regressed experimental equilibrium constant models are the same (17%) irrespective of the model used. This is because, only the equilibrium constant values for reactions (VI) and (VII) [$K_{(VI)}$ and $K_{(VII)}$] were computed directly from the models, while $K_{(V)}$ (Marshall & Franck, 1981), $K_{(VIII)}$ and $K_{(IX)}$ obtained by Baghalha & Papangelakis, (1998) from experimental fitting which considered the activity coefficients calculated from the Pitzer ion interaction model were used.

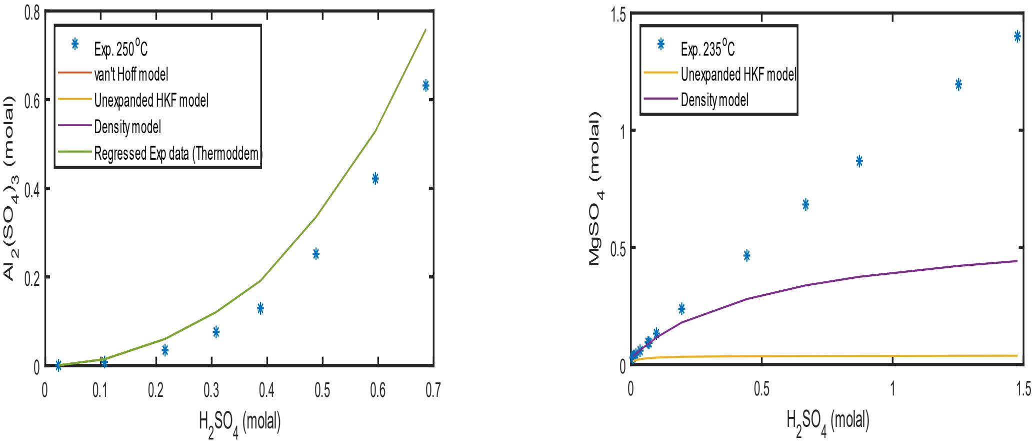

Fig. 3. Comparison of the solubility speciations of $Al_2(SO_4)_3$ at 250 °C (left) and $Mg(SO_4)$ at 235 °C (right) with different equilibrium constant models without incorporating the activity coefficient models. The term 'Regressed Exp. data' is the equilibrium constant obtained from Eq. (8)

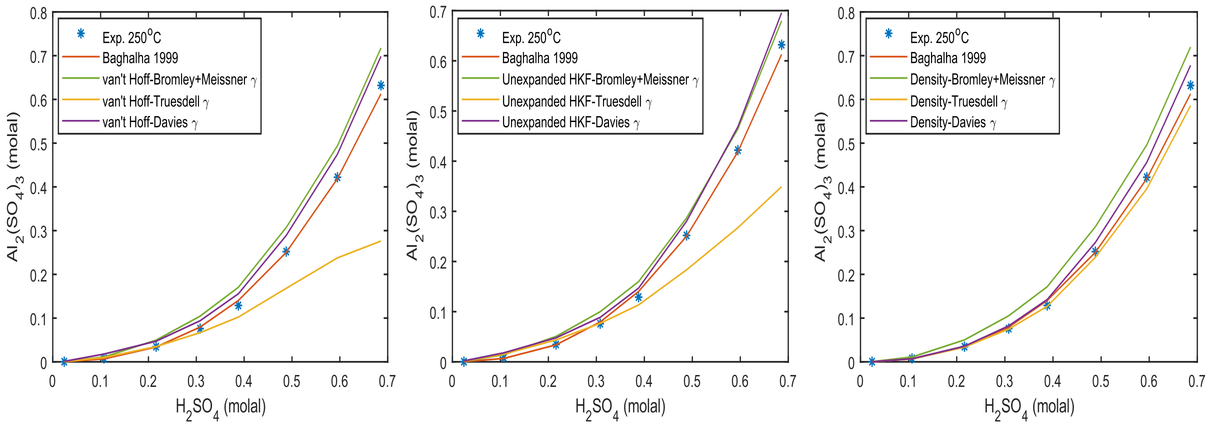

Fig. 4. Comparison of the solubility speciations of $Al_2(SO_4)_3$ with different equilibrium constants [Eqs. (5) – (8)] and activity coefficient models [Eqs. (1), (2), and (3+4)] at 250 °C.

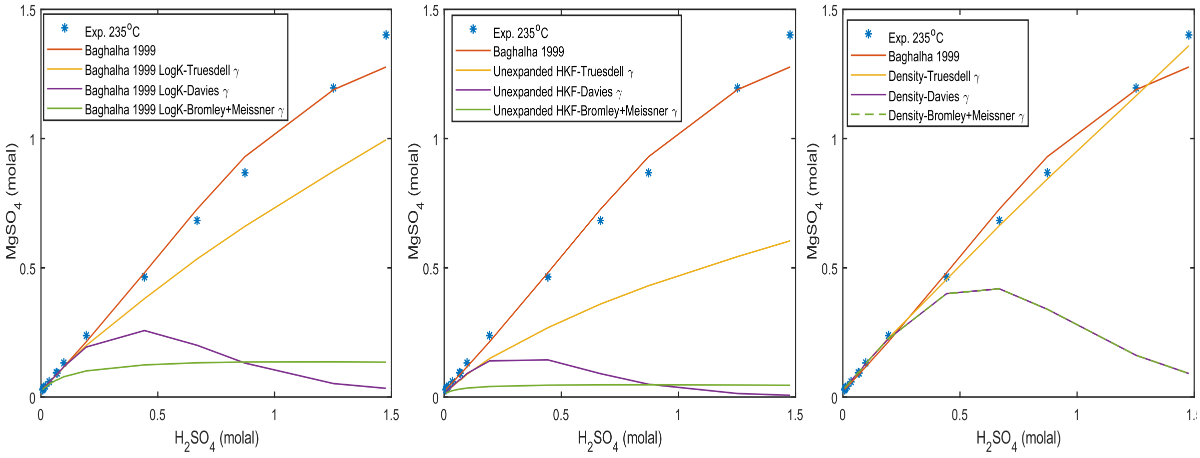

Fig. 5. Comparison of the solubility speciations of $MgSO_4$ with different equilibrium constants [Eqs. (5), and (6)] and activity coefficient models [Eqs. (1), (2), and (3+4)] at 235 °C.

Contrasting to $MgSO_4$ speciation where all the equilibrium constant values for the four reactions were obtained directly from the respective models without the activity coefficient in Fig. 3, there is a noticeable difference between the unexpanded HKF and the Density model with deviations of 97 and 69% respectively.

In the comparison of the speciation of $Al_2(SO_4)_3$, and $MgSO_4$ without the activity coefficient in Fig. 3 and with the activity coefficient in Figs. 4, and 5, the Density equilibrium constant model with the Truesdell-Jones activity coefficient model gave the best fit to the experimental data for both solubility speciations with a deviation of 7% (with the incorporation of the activity coefficient model) compared to 17% (without the incorporation of the activity coefficient model) for $Al_2(SO_4)_3$ speciation, and 3% (with the incorporation of the activity coefficient model) compared to 69% (without the incorporation of the activity coefficient model) for $MgSO_4$ speciation. This result is similar to the results obtained by Baghalha & Papangelakis, (1998) with the Pitzer activity coefficient model for $Al_2(SO_4)_3$, and even gave slightly a better fit for $MgSO_4$ speciation than the results of Baghalha & Papangelakis, (1998) when compared to the experimental data.

The Density model is more accurate in estimating the equilibrium constant of a reaction at higher temperatures (Anderson et al., 1991). The validity of the Density equilibrium constant model has been proven in different speciation studies but mainly with the Bromley activity coefficient models where the "B" parameters for the reaction species are available.

The Density equilibrium constant and Bromley activity coefficients models were used in the speciation modelling of Fe_2O_3–H_2SO_4–H_2O (Liu et al., 2003; Papangelakis et al., 2004), and $Al_2(SO_4)_3$–$MgSO_4$–$NiSO_4$–H_2SO_4–H_2O, (Papangelakis et al., 2004; Liu & Papangelakis, 2005) in the temperature range of 200 – 300 °C with the OLI® process modelling software. The "B" parameter in the Bromley equation [Eq. (3)] for each species at the modelled temperature is embedded in the software, hence, Eq. (3) was used directly without combining with Eq. (4). For each of the studied speciation modelling, the Density model proved to be a good model for the extrapolation of the equilibrium constant provided that accurate thermodynamic data (enthalpy, entropy, specific heat capacity) at the reference state are available. The results obtained showed that the modelled solubility of Fe_2O_3, $Al_2(SO_4)_3$, $MgSO_4$, and $NiSO_4$ in H_2SO_4 is in good agreement with the obtained experimental measurements for the respective species.

This paper has further shown the comparison of the Density model with other equilibrium constant models as well as compared results obtained when different activity coefficient models are incorporated with the various equilibrium constant models. The Pitzer activity coefficient model is a good model for speciation modelling for higher ionic strengths (Pitzer, 2002), but the unavailability of the parameters for most of the salt species and the complexity of the equation limits the applicability of the model.

4. Conclusions

This study presents different equilibrium constant models used to extrapolate the equilibrium constant of chemical reactions at higher temperatures. The obtained results depict that discrepancies exist between the models used for the calculation of the equilibrium constants and speciation of aqueous electrolyte solutions at high temperatures. This is mainly due to the assumptions of the model used for the computation of the equilibrium constants. It is worth noting that the extrapolation of the equilibrium constants with the models presented in this paper except Eq. (8) depends on the acquisition of reliable thermodynamic data (enthalpy, entropy, heat capacity) at the reference temperature to obtain accurate equilibrium constant values when extrapolated.

Furthermore, the activity coefficient models were incorporated in the determination of the equilibrium constant of each reaction for the speciation of H_2SO_4–$Al_2(SO_4)_3$–$MgSO_4$. The results of the speciation at 235 and 250 °C show that the activity coefficient (γ) plays a major role in the chemical speciation of aqueous solutions since it accounts for the samples' deviation from the ideal mixing behaviour in a mixture of chemical substances.

The Truesdell-Jones activity coefficient model gave the best fit to the experimental data when modelled with the regressed experimental correlation or the Density equilibrium constant model, similar to the result of Baghalha & Papangelakis, (1998) with the Pitzer activity coefficient model. The Truesdell-Jones activity coefficient model accounts for the observation that in high-ionic-strength experimental systems, the activity coefficients increase with increasing ionic strength because of the presence of bb (kg/mol) and the ionic size parameter $\dot{\alpha}$ (nm) in the equation.

The Davies model gave a good result for $Al_2(SO_4)_3$ but not for $MgSO_4$ speciation. This can be linked to the fact that the model is purely empirical and does not consider the effect of the ion interaction in the aqueous system which becomes more pronounced at higher ionic strength. The combination of the Bromley and Meissner activity coefficient model did not give a favourable result in comparison with experimental data. But, provided the "B" in Bromley's equation parameters are available and reliable, the Bromley model has been identified to give a similar result to the Pitzer model at high ionic strength (Zemaitis et al., 1986; Liu et al., 2003; Liu & Papangelakis, 2005).

The Density model with the Truesdell-Jones model yields a good result similar to the regressed experimental data correlation with a deviation of 7% and 3% at the maximum studied H_2SO_4 concentration for $Al_2(SO_4)_3$ and $MgSO_4$ speciation. Thus, the Density model has been proven as a suitable model for high-temperature equilibrium constant extrapolation when experimental data are not available. This consideration could be linked to its incorporation of the specific heat capacity and the thermal expansivity of the solution medium (e.g. water). Provided the experimental fitting parameters in Eq. (8) are available, the equation can be used to obtain the equilibrium constant of a given reaction at higher temperatures. The regressed experimental model from the Thermoddem database with the Truesdell-Jones model gave a good fit to the experimental data for the $Al_2(SO_4)_3$ speciation with a deviation of 6%. It will be recommended to use the Density equilibrium constant model with the activity coefficient models that consider the effects of ion interactions for modelling aqueous systems in areas where experimental data of a given reaction is not available.

Acknowledgements

The authors wish to thank Prony Resources, New Caledonia, Chaire MINAUMET, and the ANRT-CIFRE, France for the funding of this research.

References

ANDERSON, G. M., CASTET, S., SCHOTT, J., MESMER, R. E. (1991). *The density model for estimation of thermodynamic parameters of reactions at high temperatures and pressures*. Geochimica et Cosmochimica Acta, 55(7), Article 7. https://doi.org/10.1016/0016-7037(91)90022-W

BAGHALHA, M. (1999). *Aqueous H_2SO_4-$Al_2(SO_4)_3$-$MgSO_4$ solutions at 250°C, identification of chemistry and thermodynamics, and application to the pressure acid leaching of laterites* [Thesis].

BAGHALHA, M., PAPANGELAKIS, VLADIMIROS G. (1998). *The ion-association-interaction approach as applied to aqueous H2SO4-Al2(SO4)3-MgSO4 solutions at 250 °C.* Metallurgical and Materials Transactions B, 29(5), Article 5. https://doi.org/10.1007/s11663-998-0070-6

BROMLEY, L. A. (1973). *Thermodynamic properties of strong electrolytes in aqueous solutions*. AIChE Journal, 19(2), 313–320.

CASAS, J. M., PAPANGELAKIS, V. G., LIU, H. (2005). *Performance of Three Chemical Models on the High-Temperature Aqueous $Al_2(SO_4)_3$−$MgSO_4$−H_2SO_4−H_2O System.* Ind. Eng. Chem. Res., 44(9), 2931–2941.

COBBLE, J. W., MURRAY, R. C., JR., TURNER, P. J., CHEN, K. (1982). *High-temperature thermodynamic data for species in aqueous solution.*

DICKSON, A. G., WESOLOWSKI, D. J., PALMER, D. A., MESMER, R. E. (1990). *Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250 degree C.* Journal of Physical Chemistry; (United States), 94:20.

GULTOM, T., SIANIPAR, A. (2020). *High pressure acid leaching: A newly introduced technology in Indonesia*. IOP Conference Series: Earth and Environmental Science, 413, 012015.

HELGESON, H. C. (1967). *Thermodynamics of complex dissociation in aqueous solution at elevated temperatures. The Journal of Physical Chemistry*, 71(10), Article 10. https://doi.org/10.1021/j100869a002

HELGESON, H. C. (1981). *Prediction of the thermodynamic properties of electrolytes at high pressures and temperatures*. Physics and Chemistry of the Earth, 13–14, 133–177.

HELGESON, H. C., & KIRKHAM, D. H. (1974). *Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures; II, Debye-Huckel parameters for activity coefficients and relative partial molal properties*. American Journal of Science, 274(10), 1199–1261.

HOFF, J. H. (1896). *Studies in Chemical Dynamics*. F. Muller.

LANGMUIR, D. (1997). *Aqueous environmental geochemistry.* Prentice Hall.

LIU, H., PAPANGELAKIS, V. G. (2005). *Chemical modeling of high temperature aqueous processes.* Hydrometallurgy, 79(1), 48–61.

LIU, H., PAPANGELAKIS, V. G., ALAM, M. S., SINGH, G. (2003). *Solubility of Hematite in H2SO4 Solutions at 230-270°C.* Canadian Metallurgical Quarterly, 42(2), 199–207.

MARSHALL, W. L., FRANCK, E. U. (1981). *Ion product of water substance, 0–1000 °C, 1–10,000 bars New International Formulation and its background*. Journal of Physical and Chemical Reference Data, 10(2), 295–304.

MARSHALL, W. L., SLUSHER, R. (1965). *Aqueous Systems at High Temperature. XV. Solubility and Hydrolytic Instability of Magnesium Sulfate in Sulfuric Acid-Water and Deuterosulfuric Acid-Deuterium Oxide Solutions, 200° to 350° C.* J. Chem. Eng. Data, 10(4), 353–358.

MESHRAM, P., ABHILASH, PANDEY, B. D. (2019). *Advanced Review on Extraction of Nickel from Primary and Secondary Sources.* Mineral Processing and Extractive Metallurgy Review, 40(3), 157–193.

MOLDOVAN, M., KRUPP, E. M., HOLLIDAY, A. E., DONARD, O. F. X. (2004). *High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: A review*. Journal of Analytical Atomic Spectrometry, 19(7), 815–822.

PAPANGELAKIS, V. G., LIU, H., RUBISOV, D. H. (2004). *Solution chemistry and reactor modelling of the pal process: Successes and challenges*. International Laterite Nickel Symposium, 289–305.

PARKHURST, D. L. (1990). *Ion-Association Models and Mean Activity Coefficients of Various Salts.* In Chemical Modeling of Aqueous Systems II (Vol. 416, pp. 30–43). American Chemical Society.

PITZER, K. S. (Ed.). (1991). *Activity Coefficients in Electrolyte Solutions* (2nd ed.).

PITZER, K. S. (2002). *Thermodynamics of electrolytes. I. Theoretical basis and general equations*. In ACS Publications.

PLUMMER, N., JONES, B. F., TRUESDELL, A. H. (1976). *WATEQF; a FORTRAN IV version of WATEQ: A computer program for calculating chemical equilibrium of natural waters*. In WATEQF; a FORTRAN IV version of WATEQ : a computer program for calculating chemical equilibrium of natural waters (USGS Numbered Series No. 76–13; Water-Resources Investigations Report, Vols 76–13). Dept. of the Interior, Geological Survey, Water Resources Division,. https://doi.org/10.3133/wri7613

ROSS, C. F. (2012). 2.02—Headspace Analysis. In J. Pawliszyn (Ed.), *Comprehensive Sampling and Sample Preparation* (pp. 27–50). Academic Press. https://doi.org/10.1016/B978-0-12-381373-2.00036-3

SHOCK, E. L., HELGESON, H. C. (1988). *Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C*. Geochimica et Cosmochimica Acta, 52(8), 2009–2036.

THERMODDEM DATABASE. *Thermochemical and mineralogical tables for geochemical modeling*. Retrieved 29 June 2022, from https://thermoddem.brgm.fr/

WHITTINGTON, B. I., MUIR, D. (2000). *Pressure Acid Leaching of Nickel Laterites: A Review*. Mineral Processing and Extractive Metallurgy Review, 21(6), 527–599.

YAN, X., NI, Z. (2001). *Speciation of metals and metalloids in biomolecules by hyphenated techniques*. Guang Pu Xue Yu Guang Pu Fen Xi = Guang Pu, 21(2), 129–138.

ZEMAITIS, J. F., CLARK, D. M., RAFAL, M., SCRIVNER, N. C. (1986). *Activity Coefficients of Single Strong Electrolytes.* In Handbook of Aqueous Electrolyte Thermodynamics (pp. 46–203). John Wiley & Sons, Ltd. https://doi.org/10.1002/9780470938416.ch4

Appendix

Species parameters and equilibrium constant values used for the speciation

Table A1: Parameters for Truesdell-Jones and Bromley equations.

Species	$\dot{\alpha} \times 10^{-8}$ (cm)	b_b (kg/mol)	B (Bromley, 1973) at 25 °C
H^+	4.78	0.24	0.1905
OH^-	10.65	0.21	-0.924
SO_4^{2-}	5.31	-0.07	-0.4
HSO_4^-	4.5[W]	0.034[W]	-0.2095
Mg^{2+}	5.46, 5.5	0.22, 0.20	0.214
$MgSO^{\circ}_{4(aq)}$	3.0[C]	0.034[C]	-0.0058
Al^{3+}	6.65	0.19	0.172
$AlSO_4^+$	4.0[C]	0.0034[C]	0.004
$Al_2(SO_4)^{\circ}_{3(aq)}$	3.0[C]	0.0034[C]	-0.004

Unless otherwise stated, all $\dot{\alpha}$ and b_b data are as reported by Parkhurst (1990). The activity of water and solids are 1 and 0 respectively. C: (Casas et al., 2005); W: WATEQ4F database (Plummer et al., 1976).

Table A2: Calculated equilibrium constant values of different reactions obtained with different models

$Al_2(SO_4)_3$ speciation					
Models	Temperature (250 °C)				
	$\log(K_V)$ H_20 Reaction	$\log(K_{VI})$ HSO_4^- Reaction	$\log(K_{VII})$ $AlSO_4^+{}_{(aq)}$ Reaction	$\log(K_{VIII})$ $Al_2(SO_4)_3{}^{o}{}_{(aq)}$ Reaction	$\log(K_{IX})$ $H_3OAl_3(SO_4)_2(OH)_{6(s)}$ Reaction
Eq. (5)	-11.191 [M]	-5.845[H]	5.730[H]	2.523 [B]	1.415 [B]
Eq. (6)	-11.191 [M]	-5.827[E]	8.526[E]	2.523 [B]	1.415 [B]
Eq. (7)	-11.191 [M]	-1.995[V]	3.727[V]	2.523 [B]	1.415[B]
Eq. (8)	-11.191 [M]	-5.447[T]	9.564[T]	2.523 [B]	1.415 [B]
Baghalla (1999)	-11.191 [M]	-5.355[D]	12.000 [B]	2.523 [B]	1.415 [B]

$MgSO_4$ speciation				
Models	Temperature (235 °C)			
	$\log(K_V)$ H_20 Reaction	$\log(K_{VI})$ HSO_4^- Reaction	$\log(K_X)$ $MgSO_4{}^{o}{}_{(aq)}$ Reaction	$\log(K_{XI})$ $MgSO_4{\cdot}H_2O$ Reaction
Eq. (5)	-11.313[H]	-5.440[H]	4.308[H]	2.585[H]
Eq. (6)	-10.945[E]	-5.526[E]	4.255[E]	1.514[E]
Eq. (7)	-9.962[V]	-1.995[V]	3.218[V]	-2.680[V]
Baghalla (1999)	-11.200[M]	-5.110[D]	4.454[B]	1.664[B]

All the equilibrium constant values from van't Hoff, Unexpanded HKF and Density models were obtained with the thermodynamic data from Liu & Papangelakis, (2005) which is consistent with Shock & Helgeson, (1988). V: values calculated with the van't Hoff model, H: values obtained with the Unexpanded HKF model, E: values obtained with the Density model, B: data from Baghalha, (1999), D: data from Dickson et al., (1990) used by Baghalha & Papangelakis (1998), M: data from Marshall & Franck, (1981) used by Baghalha & Papangelakis (1998). T: values obtained with the regressed experimental model from the Thermoddem database.