Thermodynamic modeling of sulfuric acid solution using Pitzer model: sensitivity, estimability analysis and parameter identification

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Motivation

Sulfuric acid is an important component in chemical industry in general and in phosphate industry in particular. It is mainly used in the production of phosphoric acid from phosphates ore. The design and mastering of the manufacturing processes of these two acids requires an understanding of all the phenomena involved. Among them, thermodynamics plays a major role in the prediction and optimization of the process performances. This work deals with the thermodynamic modeling of sulfuric acid, based on the specific interactions model of Pitzer. The use of this kind of models requires an optimal identification of unknown parameters from experimental data. for this purpose, sensitivity and estimability analysis were used to assess parameter influences on this thermodynamic model. and to evaluate which parameters are estimable and those that can be fixed either from literature or from previous studies. Pitzer parameters were modeled as functions of the temperature. Their values were used to compare the model predictions to the experimental data. The results show finally that the models predictions are in good agreem- ent with the observed data.

Governing equations

- **Pitzer model** (Free energy of Gibbs)

$$\frac{G^{EX}}{W_n RT} = f(I) + 2\sum_c\sum_a m_c m_a \left[B_{ca} + \left(\sum_c m_c \mid z_c \mid\right) C_{ca}\right] + \sum_c\sum_{c'}\left(\theta_{cc'} + \frac{1}{2}\sum_a m_a \psi_{cc'a}\right) + \sum_a\sum_{a'}\left(\theta_{aa'} + \frac{1}{2}\sum_a m_a \psi_{aa'c}\right)$$

Subscripts c, c', and a, a' denote cations and anions present in aqueous phase. B, C, ϕ, θ and ψ are interaction parameters. f(I) is an electrostatic force expressed as function of ionic-strength.

- **Sobol method** (Total sensitivity)

$$\hat{V} = \frac{1}{N}\sum_{k=1}^{n} f(X_{k1}, X_{k2}, ..., X_{kd})^2 - \hat{f}_0{}^2$$

$$V_i = V(E[Y/Xi]) = \mathbf{E}[\mathbf{E}[Y/X_i]^2] - \mathbf{E}[\mathbf{E}[Y/X_i]]^2 = U_i - \hat{f}_0{}^2$$

$$\hat{ST}_i = 1 - \frac{U_{\sim} i - \hat{f}_0^2}{\hat{V}} \;\; and \;\; U_i = \frac{1}{N}\sum_{k=1}^{n} A_{B,k}.Y_{C_i,K}$$

k_i, V, V_i and ST_i denote respectively the model arguments, total, partial variances and total sensitivity.

- **Random Balance design** (First-order sensitivity)

$$F_i(\omega) = \frac{1}{\pi} \mid \sum_{j=1}^{N} (\psi_i^R)^{(j)} exp(-i\omega j) \mid \;\; and \;\; S_i = \frac{\sum_{j=1}^{M} F_i(j\omega)}{\sum_{j=1}^{N} F_i(j\omega)}$$

F_i, ω, and ψ denote fourier spectrum, pulsation of the periodic input, and fourier re-ordred sequence used to compute first order sensiivity.

Sensitivity analysis results

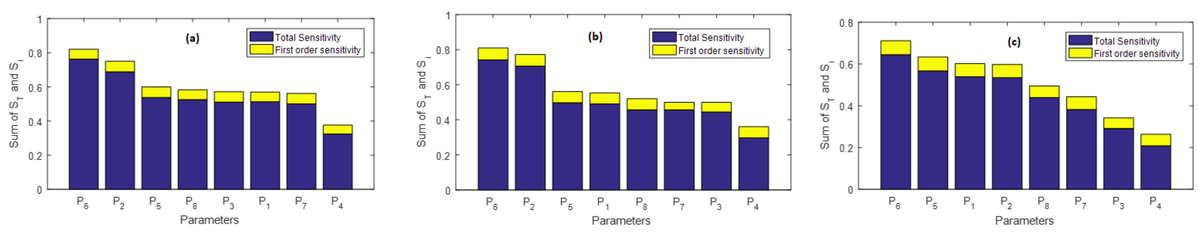

Figure: S_T and S_i for H^+ molality, **a**: C=6moles/Kg, **b**: C=3 moles/Kg, **c**: C=1mole/Kg

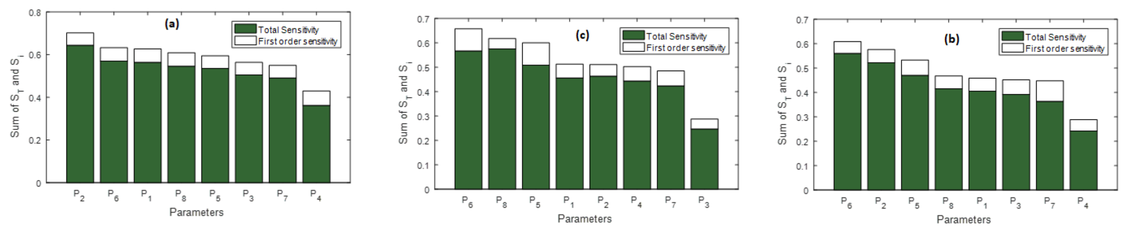

Figure: S_T and S_i for HSO_4^- molality, **a**: C=6moles/Kg, **b**: C=3 moles/Kg, **c**: C=1mole/Kg

Total and first-order sensitivity indices are used to rank the parameters in sense of their importance, this study shows that the most important interactions in the reacting medium are Cation-Anion interactions, whereas Anion-Anion interaction can be neglected.

Estimability analysis results

Estimability analysis using orthogonalization based method is used to determine the optimal and sufficient experimental measurements that allow to identify correctly pitzer parameters:

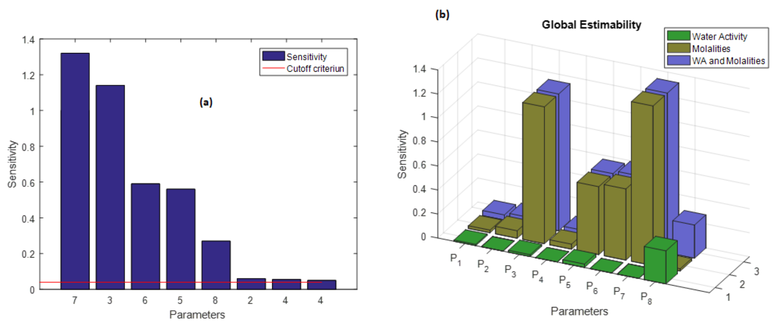

Figure: **a**: Estimability using all experimental measurements, **b**: Estimability for all cases

This study shows that the optimal and sufficient experimental measurements that allow to identify the parameters are essentially water activity and the molale concentrations of the several electrolytes present in the reacting medium. Pitzer parameters must be identified minimizing the following objective function:

$$ME = \sum_i \left(\frac{m_{H^+}^{Exp} - m_{H^+}^{Mod}}{m_{H^+}^{Exp}}\right)^2 + \left(\frac{m_{HSO_4^-}^{Exp} - m_{HSO_4^-}^{Mod}}{m_{HSO_4^-}^{Exp}}\right)^2 + \left(\frac{m_{SO_4^{2-}}^{Exp} - m_{SO_4^{2-}}^{Mod}}{m_{SO_4^{2-}}^{Exp}}\right)^2 + \left(\frac{a_{H_2O}^{Exp} - a_{H_2O}^{Mod}}{a_{H_2O}^{Exp}}\right)^2$$

ME, m_i and a_i denote respectively the mean error, molality and and water activity of the i^{th} electrolyte.

Some experimental data and models predictions

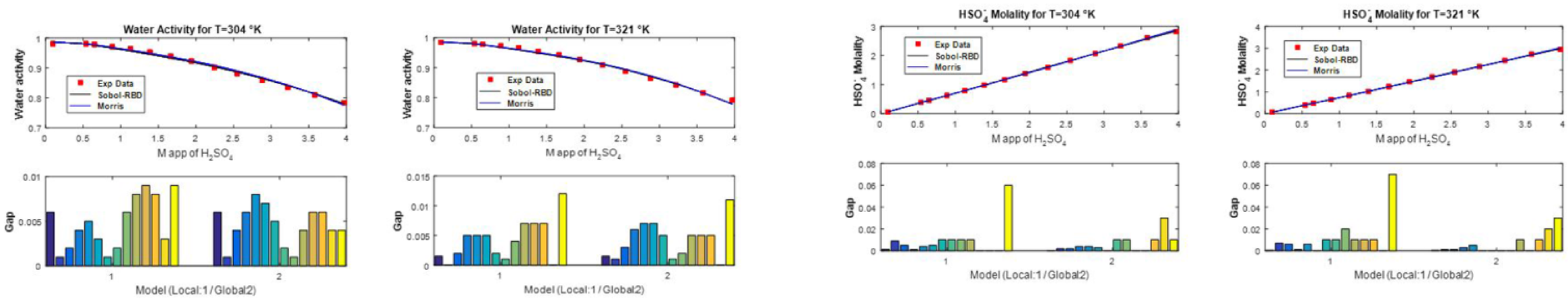

Figure: experimental data and models predictions