Pitzer ion-interaction parameters for Al(III) in the H + Na + K + Ca + Mg + Cl + H2O system up to salts solubility at 298.15 K

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INTRODUCTION

The fundamental research and economic interest of industrials for natural brines is continuously increasing all over the World. More and more substances are extracted from these brines, needing the development of specific exploitation processes. Geochemical modeling can help these industrial technologies providing robust geochemical codes and relevant databases for describing and predicting the critical chemical reactions/steps inside these specific and complex media (dissolution/ precipitation of salts, corrosion/scaling problems…).

The Pitzer approach is usually quoted to describe such complex systems but its related databases need to be continuously improved to integrate new chemical species and interaction parameters of complex aqueous systems. This study focuses on very acidic systems and on the efforts made to define the interactions of Al(III) species inside the H-Na-K-Mg-Ca-Cl-H_2O system at 25°C. This study is the continuation of a work focused on Fe(III) species in brines [1].

The Pitzer interaction parameters determined in this study allow the description of the thermodynamic behavior of ternary systems up to salt solubility. These parameters are implemented in a database adapted to the geochemical code PHREEQC [2].

DESCRIPTION OF THE WORK

The building of the database able to describe the ion-ion interactions in saline solutions needs to define specific binary and ternary interaction parameters. The developed methodology is based on a progressive approach, beginning with the determination of the ion interaction coefficients in binary systems before working on ternary systems. The equilibrium constant of salts are also integrated in this approach in order to obtain a fully internally consistent database. Some of the interaction coefficients can be issued from literature, the others being estimated or re-estimated in order to match experimentally measured data, namely: water activity, osmotic coefficients and salt solubility [3].

RESULTS

Binary systems

Osmotic coefficients of $AlCl_3$ solutions are plotted versus the salt molality on Fig. 1. It shows that the parameterizations for the $AlCl_3$-H_2O system issued from [4] match the measured values of osmotic coefficient.

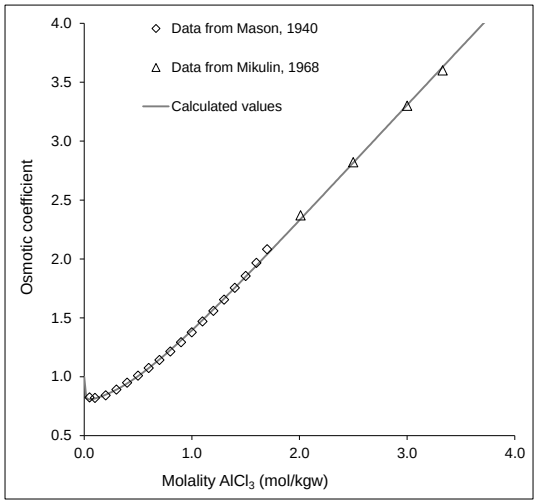

Fig. 1: Calculated (line) and experimental (symbols) water activity for the $AlCl_{3(aq)}$-H_2O binary system as a function of total molality of $AlCl_3$ at 25 °C. The maximum experimental ionic strength is about 20 eq/kg.

Ternary systems

For the K-Al-Cl system, the solubility measurements of sylvite in $AlCl_3$ solutions are selected from different authors (Fig. 2). The ternary parameters, θ and ψ, proposed by [4] do not allow reproducing the experimental data. A new parameterization has been done, leading to a good fit of the data and a correct description of the invariant point between sylvite and $AlCl_3.6H_2O_{(s)}$ (Fig. 2)

For describing the Na-Al-Cl system, Christov et al. [5] used ternary parameters from Palmer and Wesolowski [6]. With these parameters, the match between experimental and calculated data is good.

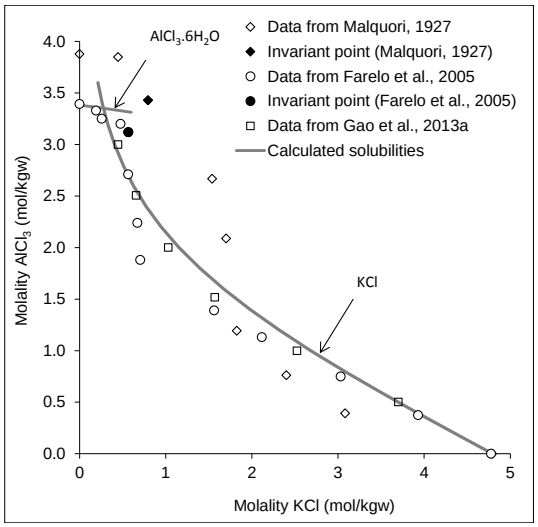

Fig. 2: Salt solubility diagrams in ($KCl+AlCl_3$) solutions at 25°C

For the Mg-Al-Cl system, the parameterization given by [4] does not allow fitting experimental data. With a revised Ψ value, the description of experimental data can be achieved (Fig. 3).

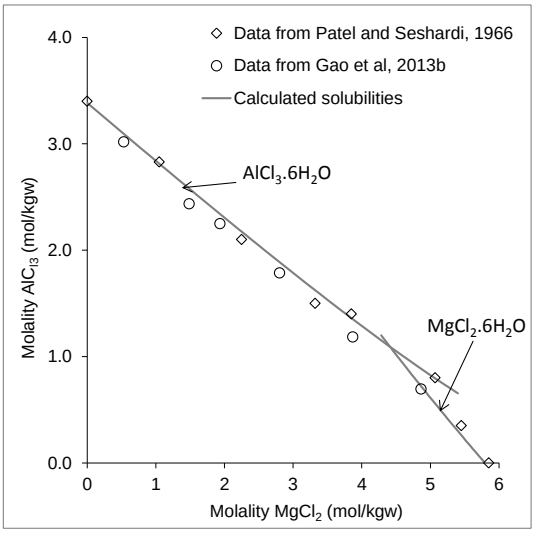

Fig. 3: Salt solubility diagrams in ($MgCl_2+AlCl_3$) solutions at 25°C

For the Ca-Al-Cl system, solubility data of antarcticite and $AlCl_3.6H_2O$(s) are from Sarkarov and Mironova [7] and Gao et al [8]. The Ψ value needed to be adjusted to match the experimental solubility data allowing then to reproducing correctly the invariant point between the two salts.

For the H-Al-Cl system, θ and ψ parameters established by [5] give an excellent fit between numerical modelling results and the experimental solubility data of $AlCl_3$:$6H_2O_{(s)}$ in HCl solutions.

CONCLUSIONS

The set of parameters established in this work is suitable to reproduce water characteristics of aluminum chloride solutions both at low and high ionic strengths. This new set of parameters can represent in particular the composition and the excess properties of aluminum in the H-Na-K-Ca-Mg-Cl-H_2O system. All binary and mixed solution interaction parameters and equilibrium constants of Al(III) minerals are coherent, and therefore can be used to determine the activities of dissolved species up to the salt solubility concentrations.

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