



Improvement of the Pitzer thermodynamic database of the EQ3/6 software package for the geochemical modeling of geological CO₂ disposal

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Carbon dioxide sequestration and storage, through injection in deep geological formations, represents a topic of worldwide interest in the context of possible actions addressed to reduce the GHG emission to the atmosphere.

Prediction of the fate of the injected CO₂ in high-temperature saline aqueous solutions, such as those hosted in sedimentary basins, and the subsequent interaction of the resulting highly reactive fluids with the reservoir formations can make use of geochemical modelling, which is a powerful technique to follow the long-term evolution of the system (Marini, 2007).

Nevertheless, geochemical modelling of brine-rock interaction under reservoir conditions is not an easy task at present for several limitations represented by the need to describe interactions among dissolved components in brines for computing their activity coefficients and to extend these interaction parameters to the pressure, temperature conditions of the reservoir.

A conspicuous number of binary interaction parameters for main dissolved cations and anions, aqueous silica and dissolved CO₂ were derived through the study of simple electrolytes but there is a general lack of information on aluminium, a component of primary interest for the geochemical modelling of geological fluids.

For instance, the Pitzer thermodynamic database YPF of the EQ3/6 software package, v. 8.0 (Wolery and Jarek, 2003) includes the Pitzer's interaction coefficients

$\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$ and C_ϕ for $\text{Na}^+\text{-Al(OH)}_4^-$ up to 100°C, whereas the θ_{ij} coefficients for $\text{Al(OH)}_4^- \text{-NO}_3^-$ and $\text{Al(OH)}_4^- \text{-OH}^-$ and the Ψ_{ijk} coefficients for $\text{Na}^+\text{-Al(OH)}_4^- \text{-NO}_3^-$ and $\text{Na}^+\text{-Al(OH)}_4^- \text{-OH}^-$ are known at 25°C only. These values were obtained from Felmy et al. (1994). Also included in YPF is the λ_{ij} parameter for $\text{O}_{2(aq)}\text{-Al}^{3+}$ from Clegg and Brimblecombe (1990).

Christov et al. (2007) have recently derived the Al^{3+} specific interactions in the binary $\text{Al-Cl-H}_2\text{O}$ and ternary $\text{Al-H-Cl-H}_2\text{O}$, $\text{Al-Na-Cl-H}_2\text{O}$ and $\text{Al-K-Cl-H}_2\text{O}$ systems to high molalities and from 0 to 100°C. This study was based on electromotive force measurement in the $\text{AlCl}_3\text{-HCl-H}_2\text{O}$ system (both new measurements carried out at temperatures of 0 to 45°C and AlCl_3 maximum concentrations close to 0.4 mol/kg and literature data of Leitzke and O'Brien [1968] obtained in the temperature range 25 to 60°C and AlCl_3 maximum concentrations close to 0.12 mol/kg), osmotic coefficient data in the $\text{AlCl}_3\text{-H}_2\text{O}$ system (from Richter et al. [2000] at 29.4 to 70.43°C and AlCl_3 maximum concentrations of 3.3 mol/kg) and solubility studies of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}_{(s)}$ in the $\text{AlCl}_3\text{-HCl-H}_2\text{O}$ system from 0 to 98°C and maximum Al concentrations close to 3.5 mol/kg.

These newly estimated Pitzer parameters for Al^{3+} were inserted in the EQ3/6 thermodynamic database in order to test its possible use (in spite of the lack of knowledge on $\text{SiO}_2\text{-Al}^{3+}$ interaction parameters) for the geochemical modelling of saline aqueous solutions, which represent the main target of geological CO_2 disposal.

References

- Christov C., Dickson A.G., Moller N. (2007) Thermodynamic modeling of aqueous aluminum chemistry and solid-liquid equilibria to high solution concentration and temperature. I. The acidic H-Al-Na-K-Cl-H₂O system from 0 to 100 °C. *J. Solution Chem.* **36**, 1495–1523.
- Clegg S.L., Brimblecombe P. (1990) The solubility and activity coefficient of oxygen in salt solutions. *Geochim. Cosmochim. Acta* **54**, 3315-3328.
- Felmy A.R., Rustad J.R., Mason M.J., De La Bretonne R. (1994) *A chemical model for the major electrolyte components of the Hanford waste tanks: the binary electrolytes in the systems: Na-NO₃-NO₂-SO₄-CO₃-F-PO₄-OH-Al(OH)₄ - H₂O*. PNNL Technical Report TWRS-PP-94-090, Pacific Northwest National Laboratory, Richland, Washington.
- Leitzke M., O'Brien H. Jr.(1968) Electromotive force studies in aqueous solutions at elevated temperatures. X. The thermodynamic properties of HCl-KCl, HCl-RbCl, HCl-CsCl, HCl-MgCl₂, HCl-CaCl₂, HCl-SrCl₂, and HCl-AlCl₃ mixtures. *J. Phys. Chem.* **72**, 4408–4414.

Marini L. (2007) *Geological sequestration of carbon dioxide: Thermodynamics, kinetics, and reaction path modeling*. Developments in Geochemistry, Elsevier Science, 453 pp.

Richter U., Brand P., Bohmhammel K., Koennecke T.(2000) Thermodynamic investigation of aqueous solutions of aluminum chloride. *J. Chem. Thermodyn.* **32**, 145–154.

Wolery T.W., Jarek R.L. (2003) *Software user's manual. EQ3/6, Version 8.0*. Sandia National Laboratories – U.S. Dept. of Energy Report