

# THERMODYNAMIC MODELING IN THE Na-NO<sub>3</sub>-SO<sub>4</sub>-Cl-OH-H<sub>2</sub>O CHEMICAL SYSTEM AT 25 °C

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In the French concept for radioactive waste disposal, long-lived intermediate-level waste (bituminous waste, for instance) and radiferous waste contain large amounts of soluble salts which are essentially composed of nitrate and sulfate. Because of their high solubility, these salts will dissolve into the pore solution coming from the concrete barrier after the closure of the disposal. Then, under repository conditions, the resulting increased ionic strength brine could migrate by diffusion through the cement barrier, potentially reach the surrounding rock and impact the physical and chemical behavior of the constituents of the host material. The extent of this impact, including the spatial extent of the saline plume, is unknown. To determine how much of an issue this is, a first step consists of correctly describing the aqueous solutions' properties and mineral solubility in the nitrate-sulfate system.

This study focuses on the Na-NO<sub>3</sub>-SO<sub>4</sub>-Cl-OH-H<sub>2</sub>O system and, in particular, on the computation of its thermodynamic properties (e.g., water activity or osmotic coefficient, and ion activity coefficients). To this end, we use the semi-empirical thermodynamic Pitzer model [1], which was developed to extend the field of application of the Debye-Hückel equations [2] only valid for a low range of molalities. The Pitzer model relies on the description of specific interactions between aqueous species that become dominant over ionic strength as concentrations increase. For one electrolyte, hypothetically totally dissociated in water, the model involves three adjustable interaction parameters ( $\beta^{(0)}_{c/a}$ ,  $\beta^{(1)}_{c/a}$  and  $C^{\phi}_{c/a}$ ). In the quaternary system, two additional specific interactions are involved and the related interaction parameters can be determined:  $\theta_{c/c'}$  or  $a/a'$  and  $\psi_{c/c'/a}$  or  $a/a'/c$ . For more complex systems, no supplementary parameters are necessary. In case the electrolyte is considered partially dissociated, neutral species,  $n$ , can be present in the aqueous solution, which implies new additional specific interactions. Thus new binary and ternary interaction parameters can be determined ( $\lambda_{nc}$ ,  $\zeta_{nca}$ ...). Consequently a step-by-step approach is necessary to study a complex chemical system. First, all the binary sub-systems are studied and binary interaction parameters are optimized, mainly on the basis of experimental osmotic coefficient data. Then, the ternary interaction parameters are determined from solubility data. Finally, quaternary systems or more can be studied.

In the case of the system of interest in this study, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaCl are considered totally dissociated whereas the partial dissociation of NaOH must be taken into account, due to its high solubility (28.3 mol·kg<sup>-1</sup> at 25 °C) [3]. So in addition to interaction parameters for NaOH-H<sub>2</sub>O, the dissociation constant of NaOH<sup>0</sup><sub>(aq)</sub> is required. The binary interaction parameters relative to the aforementioned binary systems are provided by previous studies [3–6], while ternary interaction parameters are determined in this study. Without supplementary data the phase diagram of the quaternary system Na-NO<sub>3</sub>-SO<sub>4</sub>-OH-H<sub>2</sub>O is determined (Figure 1). The comparison of numerical results with experimental observations is tricky since few data exist on this specific system [7]. Consequently, to show the coherence of the proposed parametrization on the Na-NO<sub>3</sub>-SO<sub>4</sub>-OH-H<sub>2</sub>O system, the model is extended to study the quaternary Na-NO<sub>3</sub>-SO<sub>4</sub>-Cl-H<sub>2</sub>O system. Finally, after checking binary and ternary parameters of this last system the model can correctly represent the experimental data of the Na-NO<sub>3</sub>-SO<sub>4</sub>-Cl-H<sub>2</sub>O system. This check confirms the coherence of the proposed parametrization and the accuracy of the calculations for the Na-NO<sub>3</sub>-SO<sub>4</sub>-OH-H<sub>2</sub>O system. This chemical system of interest for the waste radioactive storage was recently published [8].

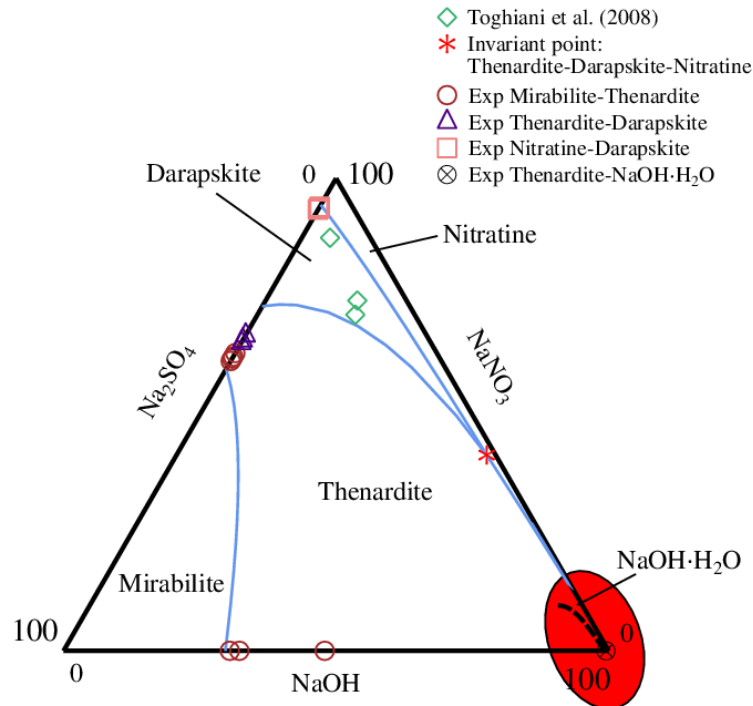


Figure 1. Solubility in the quaternary system Na-SO<sub>4</sub>-NO<sub>3</sub>-OH-H<sub>2</sub>O at T = 25 °C

- [1] K.S. Pitzer (1991) "Activity coefficients in electrolyte solutions"
- [2] P. Debye, E. Hückel (1923) "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen" Phys. Zeitschrift. 24: 185–206
- [3] A. Lach (2015) "Modélisation thermodynamique des propriétés d'excès des saumures naturelles et industrielles" thesis.
- [4] G.M. Marion (2002) "A molal-based model for strong acid chemistry at low temperatures (<200 to 298 K)" Geochim. Cosmochim. Acta. 66: 2499–2516
- [5] A. Lach, F. Boulahya, L. André, A. Lassin, M. Azaroual, J.-P. Serin, P. Cézac (2016) "Thermal and volumetric properties of complex aqueous electrolyte solutions using the Pitzer formalism - The PhreeSCALE code" Comput. Geosci. 92: 58–69
- [6] N. Møller (1988) "The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system, to high temperature and concentration" Geochim. Cosmochim. Acta. 52: 821–837
- [7] R.K. Toghiani, V.A. Phillips, L.T. Smith, J.S. Lindner (2008) "Solubility in the Na + SO<sub>4</sub> + NO<sub>3</sub> and Na + SO<sub>4</sub> + NO<sub>2</sub> Systems in Water and in Sodium Hydroxide Solutions" J. Chem. Eng. Data. 53: 798–804
- [8] A. Lach, L. André, A. Lassin (2017) "Darapskite solubility in basic solutions at 25 °C: A Pitzer model for the Na-NO<sub>3</sub>-SO<sub>4</sub>-OH-H<sub>2</sub>O system" Appl. Geochemistry. 78: 311-320