A new Pitzer parameterization for the Na-OH-Cl-NaOH0(aq)-H2O system up to high concentrations (30 M), from 0 to 250°C at water saturation pressure

Adeline Lach, Laurent André, Arnault Lassin, Mohamed Azaroual, Pierre Cézac, Jean-Paul Serin

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[1,2]A. Lach, [1]L. André, [1]A. Lassin, [1]M. Azaroual, [2]P. Cézac, [2]J.P. Serin
BRGM, D3E/BGE, 3 avenue Claude Guillemin, 45100 Orléans, France;
tel. +33 2 38 64 31 57, e-mail: A.Lach@brgm.fr; [1]BRGM, D3E/BGE, 3 avenue Claude Guillemin, 45100 Orléans, France; [2]LaTEP, UPPA, Rue Jules Ferry, 64075 Pau Cedex

The aim of this study is to represent the thermodynamic excess properties (osmotic coefficient, aqueous species and solvent activities) of Na-OH-Cl-H_2O systems from dilute to highly concentrated aqueous solutions within a 0 to 250°C temperature range at water saturation pressure. Pitzer's theory [1] was successfully used as a thermodynamic model. Binary (NaOH-H_2O) and ternary (NaOH-NaCl-H_2O) systems are successively studied in the model parameterization procedure. The binary system was already studied but not within the temperature and concentration conditions explored in this work. For the binary system two different approaches were used: (1) NaOH is completely dissociated, which requires four interaction parameters (β^0, β^1, β^2 and C^ϕ), and (2) NaOH is only partially dissociated and the neutral aqueous species $NaOH^0$(aq) and its related equilibrium dissociation constant (K_{NaOH}) are introduced in the model. Our parameterization procedure includes the following steps: first the development of the simplest model, and then progressively the increase of its complexity as long as the model is not satisfactory. Initially, we started parameters fitting using the approach (1) considering only β^0, β^1 and C^ϕ. Since model failed in reproducing the experimental thermodynamic properties correctly, we added the supplementary adjustable interaction parameter β^2 and varied the values of the associated parameter, α_2. But this last model could not still describe satisfactorily the experimental values over the whole range of concentrations and temperature of interest. Finally, we successfully applied approach (2) by introducing the temperature dependent ternary $\zeta_{Na+/OH-/NaOH}$ and binary $\lambda_{NaOH/NaOH}$ interaction parameters in addition to β^0, β^1, C^ϕ and the thermodynamic equilibrium constant (K_{NaOH}). The second approach fits better the osmotic coefficient and solvent activities up to 30 mol.kg^{-1} and to 250°C. The resulting model also allows describing the solubility of NaOH in H_2O with a very good confidence, taking into account the five hydrated states of the solid salts (NaOH:nH_2O with n=1,2,3.11,3.5 and 4) [2]. The thermodynamic solubility products of the five salts were also determined in this study. Then, we studied the solubility of NaCl in NaOH solutions and thus optimised two new temperature dependent ternary interaction parameters $\psi_{Na+/Cl-/OH-}$ and $\zeta_{Na+/OH-/NaCl}$, which are consistent with the $\theta_{Cl-/OH-}$ interaction parameter estimated by Christov and Moller [3]. The final model is able to correctly represent aqueous properties and salt solubilities in the Na-OH-Cl-$NaOH^0$(aq)-H_2O system at high concentrations and temperatures and consistently extends the model of [3].

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