Ni and Co chloride complexing in hydrothermal fluids: Spectrophotometric experiment (to 450 °C, 1 kbar) and thermodynamic model

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Stabillity of Co and Ni chloride complexes was studied using a home-maid Ti optical cell equiped with sapphire windows and connected to a Carry 4000 spectrophotometer by silica glass fiber optic. Measurements of spectra were performed up to 450 °C, 1 kbar in acidic solutions (m(HCl) = 0.15) and NaCl concentration range from 0.03 to 3 m. The spectra of Co and Ni were recorded in separate experimental series in the visible wavelength region (350 – 800 nm), the concentration of Co and Ni in the experimental solutions was 0.03m and 0.01m, respectively. In the experimantal wavelength range the optical absorbance of the experimental solutions fall within the 0 – 3.5 unit interval. The primary experimental data reduction was performed with the OptimS computer code, which is a part of the HCh software package [1]. This program optimizes the Gibbs energy and molar absorbance of aqueous species for a series of experimental solutions studied at constant pressure and temperature.

It was found that at near- and supercritical temperature (350 – 450 °C), the effect of pressure on the apparent molar absorption coefficient (ε_{app}) of Ni solutions is much more strongly pronounced than that for Co. In both systems the number of absorbing species decreases from 5 at 300 °C to 3 at t > 350 °C. In high-temperature solutions the set of complexes $MeCl_2°$, $MeCl_3^-$, and $MeCl_4^{2-}$ gives the best fit to the experimental data in both systems. The stepwise stability constant of $MeCl_4^{2-}$ is found to be independent of temperature within the experimental uncertainty, whereas $MeCl_3^-$ stepwise stability constant increases by ~ 1.5 – 2 log units when temperature increases from 350 to 450 °C. Using the calculated stability constants, a thermodynamic model for Ni and Co-Cl complexation is developed within the framework of the HKF model.

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