First experimental investigation of hydrolysis behaviour of potassium chloroplatinate in aqueous solutions at 200-600°C and 100MPa

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Cation hydrolysis is destructive to material dissolution, species stability, and chemical constituent transport in hydrothermal solutions. However, the hydrolysis behaviour of cation complex at high temperature and high pressure is poorly understood yet, which hinders us from quantitatively studying cation speciation and complexation in hydrothermal solutions. Here, we investigated, for the first time, the hydrolysis behaviour of potassium chloroplatinate (K_2PtCl_6) at 200-600°C and 100MPa to understand the thermodynamic property of quadrivalent cation in the Cl-rich hydrothermal solutions. Variable-time experiments of the chloroplatinate solutions demonstrated that the hydrolysis reactions between the Pt complex and water molecular could get equilibrium within 12 hours. Variable-temperature experiments showed that the hydrolysis reactions were enhanced with increasing temperature, which resulted in decomposition of most chloroplatinate and precipitation of most Pt. On basis of the HKF and Van't Hoff equations, we establish a linear relationship between the cumulative hydrolysis constants of K_2PtCl_6 and temperatures (T, Kelvin):

$$\ln K = (39.638 \pm 2.5184) - (47846 \pm 1597.3)/T,$$

where the $\Delta_r H_m^\Theta$ and $\Delta_r S_m^\Theta$ were calculated to be 397.8±13.28 $kJ \cdot mol^{-1}$ and 329.6±20.94 $J \cdot mol^{-1} \cdot K^{-1}$, with ΔG decreasing from 291.29$kJ \cdot mol^{-1}$ at 25°C to 44.09$kJ \cdot mol^{-1}$ at 800°C. Our experimental results suggest that the Pt-Cl complex are thermodynamically unstable at high temperature and high pressure, unless chlorine is fertile enough in hydrothermal solutions.

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