

Stability and Structure of Aqueous Sb(III) Chloride Complexes from 25 °C to 300 °C at 25 MPa

AVINAASH PERSAUD¹, DR. SWAROOP SASIDHARANPILLAI, M.SC, PH.D.¹, JENNY S. COX² AND PETER R. TREMAINE¹

¹University of Guelph

²Formerly University of Guelph

Presenting Author: tremaine@uoguelph.ca

Despite their importance in modelling the formation of antimony and antimony-bearing hydrothermal ore deposits, only a few values for the thermodynamic properties of the antimony(III) chloride and sulfide complexes have been reported above ambient conditions (Obolensky, et al. 2007). The existing thermochemical database, which extends to ~ 250 °C, and the structures of the equilibrium antimony chloride and hydroxychloride complexes, are largely based on solubility data and EXAFS studies (Pokrovski et al., 2006). In the present study, polarized Raman spectroscopy with pressure-controlled, high-pressure fused-silica capillary cells was used to identify the complexes of antimony present in highly concentrated lithium chloride solutions ($> 2 \text{ mol} \cdot \text{kg}^{-1}$) from 25 to 300 °C at 25 MPa. Vibrational band assignments were made by comparison with computational studies using Gaussian 16 (B3LYP, IEFPCM solvation model), which showed that SbCl_6^{3-} (octahedral), SbCl_4^- (see-saw) and SbCl_3^0 (trigonal pyramidal) are the predominant antimony species up to 250 °C. Quantitative speciation data from the solvent-subtracted, reduced isotropic spectra were used to determine the stepwise formation constants, $K_{3,4}$ and $K_{4,6}$, together with SIT activity coefficient model interaction parameters. Attempts to fit $K_{4,6}$ to the ionic-strength peak areas suggested that the species SbCl_6^{3-} exists as an ion pair, LiSbCl_6^{2-} whose formation constant was expressed as $K_{4,6\text{Li}^+}$. Based on the experimental equilibrium concentrations and the fitted values of $K_{3,4}$ and $K_{4,6\text{Li}^+}$, the equilibria shift towards the SbCl_4^- species with increasing temperature up to 250 °C. At temperatures above 250 °C, the configuration of SbCl_4^- transforms from the see-saw form to a previously unreported tetrahedral geometry. Measurements at lower chloride concentrations from 5 to 60 °C showed a weak band which was assigned to SbCl(OH)_2^0 , from which formation constants were determined.

References:

- Obolensky, A.A. et al. (2007) *Russ. Geol. Geophys.* **48**, 992-1001.
Pokrovski, G.S. et al. (2006) *Geochim. Cosmochim. Acta* **70**, 4196 – 4214.

Figure Caption: Reduced isotropic Raman spectrum showing the deconvoluted bands of SbCl_4^- and SbCl_3^0 at 250 °C and 25 MPa

