THE THERMODYNAMIC CHEMISTRY OF THE
AQUEOUS COPPER-AMMONIA THIOSULFATE SYSTEM

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This Thesis is presented for the degree of doctor of Philosophy of Murdoch University
Murdoch University
2006
DECLARATION

I declare that this thesis is my own account of my research and contains as its main content work that has not previously been submitted for a degree or examination at any tertiary education institution.

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______________ day of _________________ 2006
ABSTRACT

A fundamental thermodynamic study was undertaken in order to establish the speciation of copper(I) and copper(II) during the leaching and recovery of gold from thiosulfate-copper-ammonia solutions. Despite considerable research into this complex leaching system, the lack of important fundamental chemistry has delayed the implementation of the thiosulfate process as an alternative to cyanidation. Over the last two decades, research in this field has focused on the kinetics and electrochemistry of leaching, which involves the use of copper(II) as an oxidant. However, the fundamental thermodynamic data for copper(I) and copper(II) in this system is limited.

Ion association was found to significantly affect the dissociation constant of the ammonium ion in solutions containing sodium sulfate and/or sodium thiosulfate, thus influencing the free ammonia concentration in solution. These findings highlight the importance of using the correct dissociation constant value in thermodynamic studies that involve ammonia in order to obtain precise stability constants.

It has been established that the mixed-ligand complexes $\text{Cu(NH}_3\text{)(S}_2\text{O}_3\text{)}_2^{3-}$ and $\text{Cu(NH}_3\text{)(S}_2\text{O}_3\text{)}^{-}$ exist in solution and they are more stable than the other species $\text{Cu(S}_2\text{O}_3\text{)}_3^{5-}$, $\text{Cu(NH}_3\text{)}_2^{+}$ and $\text{Cu(NH}_3\text{)}_3^{+}$ at high concentrations of ammonia and/or thiosulfate. The relative proportions of each two species is dependant on the $[\text{NH}_3] : [\text{S}_2\text{O}_3^{2-}]$ ratio in solution. This is reflected in two- and three-dimensional speciation diagrams that have been constructed for typical leaching
and recovery processes using the stability constants obtained in this study. The 3-dimensional diagrams reveal subtle speciation trends that are not easily discernable from the 2-dimensional diagrams.

An investigation into the effect of high sulfate and chloride concentrations showed that these anions are not involved in the complexation with copper(I)-ammonia or copper(I)-ammonia-thiosulfate species under the experimental conditions studied. However, these anions and perchlorate formed relatively stable species with the copper(II)-ammine complexes in the absence of thiosulfate. Stability constants were obtained for the species Cu(NH$_3$)$_4$SO$_4$\(^0\), Cu(NH$_3$)$_4$Cl\(^+\) and Cu(NH$_3$)$_4$ClO$_4$\(^-\) and it is suggested that these anionic ligands form outer-sphere complexes with the Cu(NH$_3$)$_4$\(^{2+}\) ion.

Various methods of predicting stability constants for mixed-ligand complexes from those for the corresponding single ligand systems have been evaluated for this copper(I) system. Although the results have not been quantitatively accurate, the trends suggest that an appropriate method may serve as a useful qualitative tool to predict the possible existence of mixed-ligand complexes.

The combined application of 2- and 3-dimensional speciation and potential diagrams could be used as a hydrometallurgical tool in the design, optimization and control of possible future processes for the extraction of gold using thiosulfate in the presence of copper ions and ammonia. The work presented in this thesis adds to our understanding of the chemistry of copper(I) and copper(II) in this leaching system.
ACKNOWLEDGEMENTS

I would like to thank my supervisors Professor Mike Nicol and Dr Gamini Senanayake. I valued their integrity and enthusiasm and particularly Professor Nicol's sharp mind and Dr Senanayake's clarity of thinking. It has been a privilege to be working closely with these two high calibre scientists, who in their quest for furthering the knowledge of science created an energetically enjoyable atmosphere around them.

I would like to acknowledge the following,
The A.J. Parker Cooperative Research Centre for Extractive Metallurgy and Murdoch University for their financial support through the provision of a two-year partnership scholarship.
The Chemistry Centre (WA) for granting me two years leave away from work, which allowed my full dedication to this project.
The technical support and efficiency of Ken Seymour, Justin McGuinnity, Lyn Sunderland, Stewart Kelly, the staff at Murdoch University's workshop, chemical store and IT department.
Dr Sergei Pisarevsky and Mrs Lioudmila Pissarevskaja for translating Russian papers.
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SYMBOLS

$\beta$ = Cumulative stability constant of a complex.

$K$ = Step-wise formation constant.

$[\text{NH}_3]_T$ = Total ammonia concentration (M). i.e. the sum of the concentrations of protonated and aqueous ammonia i.e. $[\text{NH}_4^+] + [\text{NH}_3]$

$[\text{NH}_3]_F$ = Concentration of free or uncomplexed aqueous ammonia (M).

$[\text{NH}_3]$ = Concentration of complexed plus free aqueous ammonia (M).

$E_{\text{Cell}}$ = The measured voltage of a cell.

$I$ = Ionic strength.

$E_J$ = Junction potential.

$\text{Var}$ = varied.

$NR$ = Not reported.

$0 \text{ corr}$ = Constants corrected to zero ionic strength by the application of some theoretical or empirical formula; this procedure is not always sharply distinguished from extrapolation.

$[\text{S}_2\text{O}_3^{2-}]_{\text{free}}$ = Concentration of thiosulfate available for complex formation.