THE SOLUTION CHEMISTRY OF THE COPPER (II) - AMMONIA - THIOSULFATE AQUEOUS SYSTEM

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Abstract

The paper presents a new thermodynamic approach to studying mixed ligand complex formation reactions in multicomponent two-phase systems "solid phase - saturated aqueous solution" under real conditions.
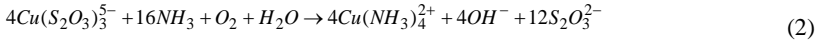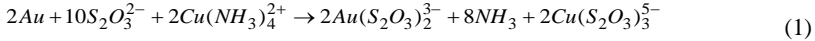
The quintessence of developed approach consists in the thermodynamic analysis of concurrent reactions in the system *Cu (II)-NH$_3$-S$_2$O$_3$$^{2-}$-H$_2$O* under real conditions on the basis of the introduced notion of the generalized reaction equation. The formation of mixed ligand complex species $Cu(OH)_i(NH_3)_j(S_2O_3)_k$ is characterized by certain peculiarities in the behavior of studied two-phase heterogeneous systems. The new feature is to focus on the chemical description of the overall process of complex formation consisting of a series of concurrent reactions, where the nature and ratio of the concentrations of chemical species, formed in such reactions, depend on the ratio of the concentrations of the metal Cu^{2+} and ligands, temperature and other factors (thermodynamic parameters).

Keywords*: ammonia, copper (II), leaching, thermodynamics, thiosulfate*

Introduction

The use of cyanide CN⁻ was the dominant method used to extract gold from its ores for many years. However, cyanide is extremely toxic to organic environments and biological creature (Xu et al 2017, Zhang & Senanayake 2016). Significant efforts candidate. This is mainly due to the fact that thiosulfate is nontoxic, inexpensive, has a good selectivity to gold with limited interference from foreign cations and high gold recoveries from a wide range of gold minerals such as ores copper, carbon blacks and sulfide ores (Abbruzzese et al 1995, Aylmore & Muir 2001a, Grosse et al 2003, Liu et al 2017). Additionally, thiosulfate has been used as a fertilizer for many years due to its relatively low impact on the environment. Various oxidants for the thiosulfate system, including oxygen, amine complexes of Cu (II), Co (III*)* amine complexes and several Fe (III) complexes (Aylmore & Muir 2001b, Liu et al 2018, Muir & Aylmore 2005, Senanayake & Zhang 2012) have been recommended. But the Cu (II) amine complexes have been studied most intensely, potentially leading to enhancement of copper concentrations in solution. Additionally, as the leach solutions should be alkaline in order to avoid thiosulfate decomposition, the addition of ammonia is required to stabilise the copper (II) as a copper (II) – ammine complex (Breuer & Jeffrey 2003).

The overall reaction of gold leaching is Au + Cu (II) = Au(I) + Cu(I). Oxidation of metallic gold in Au^+ in ammonium thiosulfate solution in the presence of Cu(II) takes place at the potential of ~ 0 V (relative to the standard hydrogen potential) and can be represented by the following equations (Wan 1997):

$$2Au + 10S_2O_3^{2-} + 2Cu(NH_3)_4^{2+} \rightarrow 2Au(S_2O_3)_2^{3-} + 8NH_3 + 2Cu(S_2O_3)_3^{5-} \tag{1}$$

$$4Cu(S_2O_3)_3^{5-} + 16NH_3 + O_2 + H_2O \rightarrow 4Cu(NH_3)_4^{2+} + 4OH^- + 12S_2O_3^{2-} \tag{2}$$

However, the mechanism of reduction of Cu(II) in Cu(I) illustrated in equations (3), (4), (5) and (6) is much more complex and involves the formation of mixed compounds in the Cu(II)-NH_3-$S_2O_3^{2-}$, Cu(I)-NH_3-$S_2O_3^{2-}$ and Au(I)-NH_3-$S_2O_3^{2-}$ systems and their adsorption on the surface of gold with the simultaneous oxidation of gold and thiosulfate (Senanayake 2004, Senanayake 2005, Choo & Jeffrey 2004). It has been shown recently that the presence of Cu (II) in the thiosulfate leach solution does not only act as an oxidant, but in addition considerably enhances the gold oxidation reaction (Breuer & Jeffrey 2003). Despite considerable research in the thiosulfate –copper – ammonia leaching system, the lack of important formal chemical thermodynamics has delayed the use of the thiosulfate process as an alternative to cyanidation. The paper presents a developed thermodynamic approach to studying mixed ligand complex formation reactions in multicomponent two-phase systems "solid phase - saturated aqueous solution" under real conditions.

Its quintessence consists in the thermodynamic analysis of concurrent reactions in the system Cu (II)-NH_3-$S_2O_3^{2-}$-H_2O under real conditions on the basis of the introduced notion of the generalized reaction equation (GRE). The formation of mixed ligand complex species $Cu(OH)_i(NH_3)_j(S_2O_3)_k$ is characterized by certain peculiarities in the behavior of studied two-phase heterogeneous systems. The new feature is to focus on the chemical description of the overall process of mixed complex formation consisting of a series of concurrent reactions, where the nature and ratio of the concentrations of chemical species, formed in such reactions, depend on the ratio of the concentrations of the metal Cu^{2+} and ligands, temperature and other factors (thermodynamic parameters).

Materials and Methods

The overall process, e.g. possible homogeneous chemical equilibria, considering all potential Cu(II) species (parent and mixed hydroxo complexes of readily hydrolysable copper ions, tris complexes in the case of large ligand excesses, precipitation etc.), can be described by the following GRE equation (the quantity f_{ijk} denotes the partial molar fraction of the respective species) (Povar et al 2018):

$$Cu^{2+} + \sum_{i=0}\sum_{j=0}\sum_{k=0} if_{ijk}H_2O + \sum_{i=0}\sum_{j=0}\sum_{k=0} jf_{ijk}\left(f_{NH_3} + f_{NH_4^+}\right)NH_3 +$$

$$\left(\sum_{i=0}\sum_{j=0}\sum_{k=0} kf_{ijk}\right)\left(\sum_{l=0} f_l H_l S_2O_3\right) = \sum_{i=0}\sum_{j=0}\sum_{k=0} f_{ijk}Cu(OH)_i(NH_3)_j(S_2O_3)_k + \tag{3}$$

$$\sum_{i=0}\sum_{j=0}\sum_{k=0} if_{ijk}H^+,$$

where $\sum_{i=0}\sum_{j=0}\sum_{k=0} f_{ijk} = 1$, $f_{NH_3} + f_{NH_4^+} = 1$ and $\sum_{l=0} f_l H_l S_2O_3 = 1$.

GRE is the generalization of a set of common chemical equations, taking into account the simultaneous formation of several different chemical species.

The mass balance equations for the investigated system are as follows:

$$C^0_{Cu^{2+}} = \sum_{i=0} \sum_{j=0} \sum_{k=0} [Cu(OH)_i[NH_3]_j[S_2O_3]_k = [Cu^{2+}]\alpha_{Cu^{2+}} \tag{4}$$

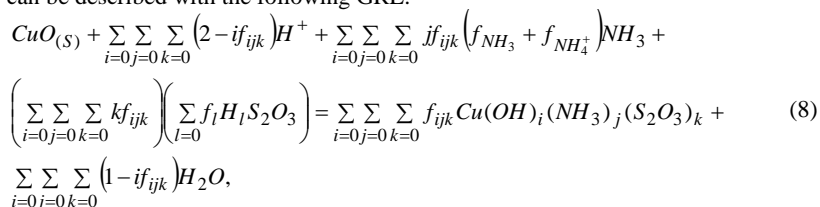$$C^0_{NH_3} = [NH_3] + [NH_4^+] + \sum_{i=0} \sum_{j=0} \sum_{k=0} j[Cu(OH)_i[NH_3]_j[S_2O_3]_k \tag{5}$$

$$C^0_{S_2O_3^{2-}} = [S_2O_3^{2-}] + [HS_2O_3^-] + [H_2S_2O_3] + \sum_{i=0} \sum_{j=0} \sum_{k=0} k[Cu(OH)_i[NH_3]_j[S_2O_3]_k \tag{6}$$

where the alpha coefficient is calculated with the deduced expression:

$$\alpha_{Cu^{2+}} = 1 + \sum_{i=0} \sum_{j=0} \sum_{k=0} \beta_{ijk}[H^+]^{-i}[NH_3]^j[S_2O_3^{2-}]^k \tag{7}$$

On the other hand, the precipitation-dissolution heterogeneous process of the slightly soluble $CuO_{(S)}$ oxide in the thiosulfate – copper – ammonia leaching system can be described with the following GRE:

$$CuO_{(S)} + \sum_{i=0}\sum_{j=0}\sum_{k=0} \left(2 - if_{ijk}\right)H^+ + \sum_{i=0}\sum_{j=0}\sum_{k=0} if_{ijk}\left(f_{NH_3} + f_{NH_4^+}\right)NH_3 +$$

$$\left(\sum_{i=0}\sum_{j=0}\sum_{k=0} kf_{ijk}\right)\left(\sum_{l=0} f_l H_l S_2 O_3\right) = \sum_{i=0}\sum_{j=0}\sum_{k=0} f_{ijk} Cu(OH)_i(NH_3)_j(S_2O_3)_k + \tag{8}$$

$$\sum_{i=0}\sum_{j=0}\sum_{k=0} \left(1 - if_{ijk}\right)H_2O,$$

The variation in Gibbs energy of the heterogeneous process (8) was calculated by means of the expression (Povar & Rusu 2012); (Povar & Spinu 2014); (Spinu 2014):

$$\Delta G = -RT \ln K_S \alpha_{Cu^{2+}} + RT \ln C^0_{Cu^{2+}}[H^+]^{-2} \tag{9}$$

where K_S is the equilibrium constant of the reaction:

$$CuO_{(S)} + 2H^+ = Cu^{2+} + H_2O, \qquad K_S = [Cu^{2+}]/[H^+]^2$$
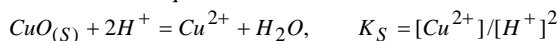
Results and Discussion
Based on the equations (1)-(9), a thermodynamic study was carried out to determine the copper (II) species during gold extraction and recovery of the copper - thiosulfate - ammonia systems. The equilibrium constants of all the possible reactions in the investigated system are summarized in Table 1. The distribution of soluble and insoluble copper species in the system $Cu(II)-NH_3-S_2O_3^{2-}$ was investigated as a function of pH, copper, ammonia and thiosulfate concentrations using the thermodynamic analysis and the repartition diagrams for heterogeneous system (Povar & Rusu 2012). The area of thermodynamic stability of the solid phase $CuO_{(S)}$ and relative amounts of each species depend on the $[NH_3]: [S_2O_3^{2-}]$ ratio in solution. Figure 1 shows that $CuO_{(S)}$ is precipitated at pH = 12.64 at high concentrations of ligands NH_3 and $S_2O_3^{2-}$ (curve 1). Our calculations showed that the

domain of stability of solid cupric oxide is expanding to lower and higher pH values with increasing Cu (II) concentrationin the manner predicted by thermodynamic modelling. The area of thermodynamic stability of cupric oxide substantially extends also with decreasing the concentrations of both ligands NH_3 and $S_2O_3^{2-}$ at the same initial concentration of Cu^{2+} (curves 2 and 3). The thermodynamic speciation of copper species shown as a function of pH in figure 2 and figure 3 was calculated based on the thermodynamic method and diagrams of heterogeneous equilibria developed by (Povar & Rusu 2012, Spinu 2014). The cupric oxide becomes the dominant species up to pH 8 at lower concentration of NH_3 and high concentration of $S_2O_3^{2-}$, prevailing over the mixed species $Cu(NH_3)_2(S_2O_3)_2^{2-}$ (Figure 3).

The thermodynamic analysis has proved that the mixed-ligand complexes $Cu(NH_3)_2(S_2O_3)_2^{2-}$ and $Cu(NH_3)_3(S_2O_3)_2^0$ are more stable and dominant than other species $Cu(S_2O_3)_k^{2-2k}$, $Cu(NH_3)_j^{2+}$ at high concentrations of ammonia and/or thiosulfate (Figure 2 and Figure 3). These results should be mandatorily taken into account at studying the redox processes of the ammoniacal thiosulfate leaching of gold.
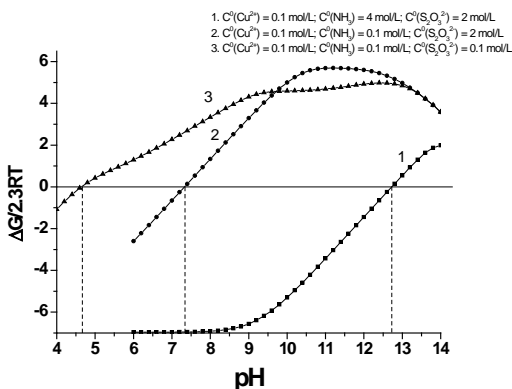

Figure 1. The variation of Gibbs energy versus pH in the heterogeneous system Cu(II)-NH_3-$S_2O_3^{2-}$-H_2O.

Table 1. The equilibrium constants of all the possible reactions in the investigated system

Species	log K	Source
$Cu(NH_3)(OH)^+$	0.9	Senanayake 2004[a]
$Cu(NH_3)_2(OH)_2$	-12.3	Senanayake 2004[a]
$Cu(NH_3)(OH)_3^-$	-25.7	Senanayake 2004[a]
$Cu(NH_3)^{2+}$	4.2	Vazquez-Arenas et al 2007
$Cu(NH_3)_2^{2+}$	7.75	Vazquez-Arenas et al 2007
$Cu(NH_3)_3^{2+}$	10.6	Vazquez-Arenas et al 2007
$Cu(NH_3)_4^{2+}$	12.9	Vazquez-Arenas et al 2007
$Cu(NH_3)_5^{2+}$	12.43	Vazquez-Arenas et al 2007
$Cu(NH_3)_2(S_2O_3)$	13.17	Senanayake & Zhang 2012
$Cu(NH_3)_3(S_2O_3)$	13.65	Senanayake & Zhang 2012
$Cu(NH_3)_2(S_2O_3)_2^{2-}$	15.06	Senanayake & Zhang 2012
$Cu(S_2O_3)$	2.4	Senanayake & Zhang 2012
$Cu(S_2O_3)_2^{2-}$	5.2	Senanayake & Zhang 2012
NH_4^+	9.4	Vazquez-Arenas et al 2007
$HS_2O_3^-$	1.68[a]	Aylmore & Muir 2001[b]
$H_2S_2O_3$	1.98[a]	Aylmore & Muir 2001[b]
$CuOH^+$	-7.7	Smith &Martell 1976[c]
$Cu(OH)_{2(aq)}$	-15.2	Smith &Martell 1976[c]
$Cu(OH)_3^-$	-27.5	Smith &Martell 1976[c]
$Cu(OH)_4^{2-}$	-40.4	Smith &Martell 1976
$CuO_{(s)}$	8.49	Plyasunova et al 1997
$Cu(OH)_{2(s)}$	9.1	Plyasunova et al 1997

[a]Recalculated for the reaction: $Cu^{2+} + iNH_3 + jH_2O = Cu(NH_3)_i(OH)_j + jH^+$

[b]Recalculated from the $\Delta G_f^0(i)$ values from CODATA recommendations.

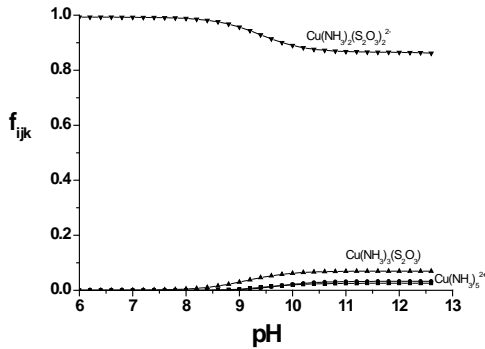[c]Recalculated for the reactions of hydrolysis.

Figure 2. Thermodynamic speciation diagram of Cu(II) species as a function of pH in the homogeneous system Cu(II)-NH$_3$-S$_2$O$_3{}^{2-}$-H$_2$O. Concentrations, mol/L: $C^0_{Cu^{2+}} = 0.1$; $C^0_{NH_3} = 4$; $C^0_{S_2O_3^{2-}} = 2$
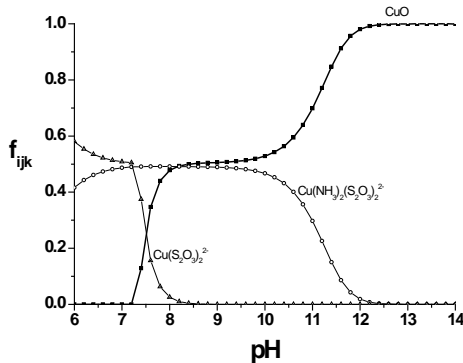
Figure 3. Thermodynamic speciation diagram of Cu (II) species as a function of pH in the heterogeneous system Cu (II)-NH$_3$-S$_2$O$_3{}^{2-}$-H$_2$O. Concentrations, mol/L: $C^0_{Cu^{2+}} = 0.1$; $C^0_{NH_3} = 0.1$; $C^1_{S_2O_3^{2-}} = 2$

Conclusions

An original thermodynamic approach to complex chemical equilibrium analysis was used, taking into account complex reactions in multicomponent heterogeneous systems under real conditions. Its principle consists in the thermodynamic analysis of the conditions of realization of different processes based on the global thermodynamic characteristics. The reciprocal relations of thermodynamic characteristics for technological processes with different physicochemical properties constitute the basis of the systematization of the experimental material, the fundamental search for the optimal conditions of technological processes or the suppression of unwanted processes.

The generalized equations of the soluble and insoluble species involved in the complex homogeneous and heterogeneous process and the equation for calculating the Gibbs energy variation of the precipitation-dissolving process of the less soluble $CuO_{(S)}$ oxide were deduced.

A thermodynamic study was accomplished to determine the copper (II) species during gold extraction and recovery with the copper - thiosulfate - ammonia systems. It has been shown that mixed complexes containing two ligands $Cu(NH_3)_2(S_2O_3)_2^{2-}$ and $Cu(NH_3)_3(S_2O_3)$ are more stable than other species as $Cu(S_2O_3)_i^{2-2i}$ and $Cu(NH_3)_j^{2+}$ at high concentrations of ammonia and/or thiosulfate.

The relative quantities of each species depend on the ratio $[NH_3]:[S_2O_3^{2-}]$ in the solution.

The thermodynamic stability of the solid phase $CuO_{(S)}$ depends greatly on the pH and concentrations of ammonia and thiosulfate.

The obtained results are useful for optimization of the overall scheme of thiosulfate leaching for gold hydrometallurgy. The speciation of copper in such complex system can have a detrimental effect on the environment as well as in the industrial processes. The precipitation of cupric oxide above a critical pH can be used in the treatment of Cu^{2+}-containing wastewater.

References

Abbruzzese, C, Fornari, P, Massidda, R, Veglio, F & Ubaldini, S 1995, 'Thiosulfate leaching for gold hydrometallurgy', *Hydrometallurgy*, vol. 39, pp. 265-276.

Aylmore, MG & Muir, DM 2001, 'Thermodynamic analysis of gold leaching by ammoniacal thiosulfate using Eh/pH and speciation diagrams', *Minerals and Metallurgical Processing*, vol. 18, no. 4, pp. 221-227.

Aylmore, MG & Muir, DM 2001, 'Thiosulfate leaching of gold - A review', *Minerals Engineering*, vol. 14, no. 2, pp. 135-174.

Breuer, PL & Jeffrey, MI 2003, 'The Reduction of Copper(II) and the Oxidation of Thiosulfate and Oxysulfur Anions in Gold Leaching Solutions', *Hydrometallurgy*, vol. 70, pp. 163-173.

Choo, WL & Jeffrey, MI 2004, 'An electrochemical study of copper cementation of gold (I) thiosulfate', *Hydrometallurgy*, vol. 71, no. 3-4, pp. 351-362.

Grosse, AC, Dicinoski, GW, Shaw, MJ & Haddad, PR 2003, 'Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review)', *Hydrometallurgy*, vol. 69, no. 1-3, pp. 1-21.

Liu, X, Xu, B, Min, X, Li, Q, Yang, Y, Jiang, T, He, Y & Zhang, X 2017, 'Effect of pyrite on thiosulfate leaching of gold and the role of ammonium alcohol polyvinyl phosphate (AAPP) ', *Metals*, vol. 7, no. 7, pp. 278-295.

Liu, X, Xu, B, Yang, Y, Li, Q, Jiang, T & He, Y 2018, 'Thermodynamic analysis of ammoniacal thiosulphate leaching of gold catalysed by Co (III)/Co (II) using E h-pH and speciation diagrams', *Hydrometallurgy*, vol. 178, pp. 240-249.

Muir, DM & Aylmore, MG 2005, 'Thiosulfate as an alternative lixiviant to cyanide for gold ores'. In: Adams, M. (Ed.) *Development in Mineral Processing*, vol. 15, Elsevier, Sydney, pp. 541-559.

Plyasunova, NV, Wang, M, Zhang, Y & Muhammed, M 1997, 'Critical evaluation of thermodynamics of complex formation of metal ions in aqueous solutions II. Hydrolysis and hydroxo-complexes of Cu^{2+} at 298.15 K', *Hydrometallurgy*, vol. 45, no. 1-2, pp. 37-51.

Povar, I & Rusu, V 2012, 'Aluminium heterogeneous speciation in natural waters', *Canadian Journal of Chemistry*, vol. 90, no. 4, pp. 326-332.

Povar, I, Spinu O & Pintilie B 2018, 'Expressions for enthalpies of concurrently polynuclear complex formation reactions in two-phase aqueous systems', *Journal of Solution Chemistry*, accepted for publication.

Povar, I & Spinu, O 2014, 'The role of hydroxy aluminium sulfate minerals in controlling Al^{3+} concentration and speciation in acidic soils', *Open Chemistry*, vol. 12, no. 8, pp. 877-885.

Senanayake, G & Zhang, XM 2012, 'Gold leaching by copper (II) in ammoniacal thiosulfate solutions in the presence of additives. Part II: Effect of residual Cu (II), pH and redox potentials on reactivity of colloidal gold', *Hydrometallurgy*, vol. 115-116, pp. 1-40.

Senanayake, G 2004, 'Analysis of reaction kinetics, speciation and mechanism of gold leaching and thiosulfate oxidation by ammoniacal copper (II) solutions', *Hydrometallurgy*, vol. 75, pp. 55-75.

Senanayake, G 2005, 'The role of ligands and oxidants in thiosulfate leaching of gold', *Gold Bulletin,* vol. 38, no. 4, pp. 170-179.

Smith, R & Martell, A 1976, *Critical stability constants*, Springer, New York.

Spinu, O 2014, 'Distribution of soluble and insoluble chemical species of chromium (III) and (VI) in aqueous solutions', *Chemistry Journal of Moldova,* vol. 9, no. 2, pp. 19-25.

Vazquez-Arenas, J, Lazaro, I & Cruz, R 2007, 'Electrochemical study of binary and ternary copper complexes in ammonia-chloride medium', *Electrochimica acta*, vol. 52, no. 20, pp. 6106-6117.

Wan, RY 1997, 'Importance of solution chemistry for thiosulfate leaching of gold'. *Proceedings of the World Gold 97*, Singapore, Society for Mining, Metallurgy and Exploration, Inc, Littleton, CO, pp. 159-162.

Xu, B, Kong, W, Li, Q, Yang, Y, Jiang, T& Liu, X 2017, 'A review of thiosulfate leaching of gold: Focus on thiosulfate consumption and gold recovery from pregnant solution', *Metals*, vol. 7, no. 6, pp. 222.

Zhang, XM & Senanayake, G 2016, 'A review of ammoniacal thiosulfate leaching of gold: An update useful for further research in non-cyanide gold lixiviants', *Mineral Processing and Extractive Metallurgy Review*, vol. 37, no. 6, pp. 385-411.