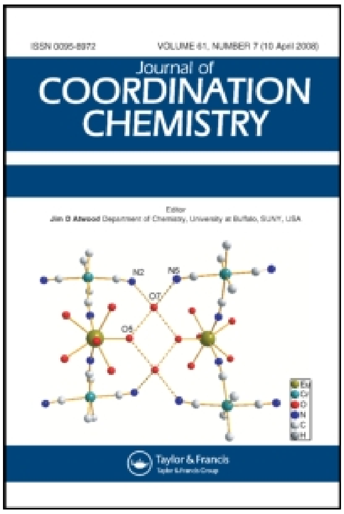

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Potentiometric study of silver complexes with thiourea in acid media

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Formation of silver complexes with thiourea in three different acids (perchloric, methanesulfonic, and sulfamic) was studied potentiometrically using modified Leden's method. It was established that, under conditions similar to the ones used for commercial electroplating of silver alloys, silver and thiourea form predominantly binuclear complexes Ag_2tu_n ($n = 1$–6). Calculated complex stability constants were similar in all cases suggesting that the acidity and the type of anion have little effect on the structure.

Keywords: Silver; Thiourea; Potentiometric titration; Binuclear complexes; Acid medium

1. Introduction

Amid growing environmental concerns the EU adopted a WEEE (Waste Directive on Electronic and Electronic Components) directive, which recommends banning lead-containing materials from the electronics industry [1]. This EU directive especially affects the usage of solder materials, since up to now lead-tin alloy was used exclusively. New, lead-free alloys as substitutes for currently used ones are thus needed.

One of the most promising candidates is Sn–Ag (2wt. % Ag) alloy, which can be obtained both metallurgically and electrolytically. During the electrochemical deposition of this alloy, ligands that form complexes with Ag and reduce the difference between electrochemical potentials of the two metals are used. Thiourea (tu) is one of the best complexing agents for this purpose in acid medium [2], since it acts in several ways [3]. Reports discussing Ag complexes with tu in acid media are rather limited with only perchloric [4–6] and nitric [7, 8] studied extensively. Silver bonds to thiourea molecule via sulfur atom, but with diverse reports in the literature. The majority of studies report mononuclear complexes [4, 8–11], although

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some authors also report binuclear complexes [5, 6, 12–14] or, under special conditions, even polynuclear complexes [7, 8, 12, 15, 16].

Plating baths formulated with methanesulfonic (HSO_3CH_3) and sulfamic (HSO_3NH_2) acids have become increasingly popular for electroplating of Sn and its alloys. These acids are biologically degradable, toxicologically safe, and also less corrosive than previously used ones. Additional introduction of silver ions and thiourea could benefit electrodeposition of Sn–Ag alloys. Unfortunately, we could not find any information about Ag–tu complexes in methanesulfonic and sulfamic acids. The goal of this study was, therefore, to investigate stability and stoichiometry of Ag complexes with tu in sulfamic and methanesulfonic solutions by potentiometric titration, under conditions similar to the ones used for electroplating of silver alloys. We have also examined Ag–tu complexes in perchloric acid solutions, since this system has been extensively covered in the literature and could be used for comparison.

2. Experimental

"Chemically pure" grade substances were used in this work. All substances were used as purchased, except for silver salts that were prepared in the lab. All solutions were prepared using triply distilled water.

The distribution of silver complexes and their stability was investigated potentiometrically using a P-5848 potentiostat (Belarus). Potentiometric measurements were conducted in a 30 mL glass cell consisting of two separated parts. Prior to measurements all solutions were deaerated with Ar for 15 min. High purity Ag strip ($0.5 \times 2\,cm^2$) was used as a working electrode. A H^+/H_2 electrode in the same acid, placed in a separate compartment and connected through a Luggin capillary, was used as a reference electrode. All potentials reported are given with respect to reference hydrogen electrode. All measurements were carried out at 20°C.

The ionic strength of all solutions was kept constant at $I = 1.5$, similar to that used in industry. Initial solutions were prepared by introducing known amounts of silver salt (C_{Ag} varied from 10^{-4} M to 0.01 M) and that of corresponding acid (0.1 M and 1 M). Finally, calculated amount of corresponding potassium salt was added to this solution to make the total concentration equal to 1.5 M. Solution, used for titration, consisted of known concentration of thiourea (typically 5 to 50 times more than C_{Ag}), corresponding amount of acid, and calculated amount of potassium salt to make total concentration equal to 1.5 M. Although, upon formation of silver-thiourea complexes, the overall concentration changes; this variation can be neglected due to large excess of buffer salt. Titration for each set of results was conducted at least twice.

2.1. *Preparation of silver methanesulfonate, silver sulfamate, and silver perchlorate*

Initially, known amount of Ag(I) nitrate was dissolved in water and slight excess of KOH solution was then added in order to form Ag_2O precipitate. Formed precipitate was thoroughly washed with CO_2– free triply distilled water and dried overnight. Silver oxide was dissolved in methanesulfonic, sulfamic, or perchloric acid in order to form corresponding salts.

2.2. *The reversibility of silver electrode*

The potential of silver electrode was reversible and determined by the concentration of free Ag^+ ions. In deaerated solution the weight of silver electrode remained constant in time and its potential was not affected by stirring. At constant ionic strength $I = 1.5\,M$, the activity coefficient of Ag^+ was dependent on the nature of ions in solution and/or acidity. The activity coefficients of Ag^+ ions were 0.5 in 0.1 M $HClO_4$, 0.6 in 1 M $HClO_4$, 0.4 in 0.1 M HSO_3NH_2, and 0.5 in 1 M HSO_3NH_2 solutions, respectively. The activity coefficient of Ag^+ ions in HSO_3CH_3 solutions was close to 1. Despite the fact that activity coefficients were different, linear dependence of E-log C_{Ag+} was observed in all cases.

2.3. *Computation of complex stability constants*

Stability constants of mononuclear complexes $Agtu_n^+$ were calculated using the method first introduced by Leden [17], based on iterative calculation of the function F(tu):

$$F(\mathrm{tu}) = \sum \beta_i [\mathrm{tu}]^{i-1} = \frac{C_{\mathrm{Ag}} - [\mathrm{Ag}^+]}{[\mathrm{Ag}^+] \times [\mathrm{tu}]} \tag{1}$$

where C_{Ag} was the total concentration of Ag^+ ions, $[Ag^+]$ and [tu] were equilibrium concentrations of Ag^+ ions and thiourea, respectively. The equilibrium concentration of silver ions was calculated by measuring the potential of silver electrode in the solution. The equilibrium concentration of thiourea was calculated from the formula:

$$[\mathrm{tu}] = C_{\mathrm{tu}} - N(C_{\mathrm{Ag}} - [\mathrm{Ag}^+]) \tag{2}$$

where C_{tu} was the total concentration of thiourea and N was average ligand number. Initially average ligand number N was calculated from:

$$N = \frac{E_I - E_{II}}{RT/F[\ln(C_{\mathrm{tu}})_{\mathrm{I}} - \ln(C_{\mathrm{tu}})_{\mathrm{II}}]} \tag{3}$$

Function F(tu) was then plotted *versus* equilibrium concentration of thiourea, [tu]. Extrapolation to $[\mathrm{tu}] = 0$ gives β_1. Second stability constant β_2 was calculated by plotting $((F(\mathrm{tu}) - \beta_1)/[\mathrm{tu}])$ *versus* [tu] and extrapolating to value of $[\mathrm{tu}] = 0$. Further stability constants were calculated in similar fashion.

In subsequent iterations N was calculated using complex stability constants determined previously according to formula:

$$N = \frac{\sum i\beta_i [\mathrm{tu}]^{i-1}}{\sum \beta_i [\mathrm{tu}]^{i-1}} \tag{4}$$

Iterations were repeated in this way until values for all stability constants did not vary.

Stability constants of binuclear complexes $Ag_2tu_n^{2+}$ were calculated in two steps. Initially the values of complexes $Ag_2tu_n^{2+}$ ($n = 1, 2, 3, 4$) were estimated using a nonlinear curve fitting algorithm incorporated into SigmaPlot 8.0 [18]. In the second step, stability constants were calculated using modified Leden's method. In this case function equations (1) and (2) transformed into equations (5) and (6), respectively:

$$F(\mathrm{tu}) = \sum \beta_i [\mathrm{tu}]^{i-1} = \frac{C_{\mathrm{Ag}} - [\mathrm{Ag}^+]}{2 \times [\mathrm{Ag}^+]^2 \times [\mathrm{tu}]} \tag{5}$$

$$[\mathrm{tu}] = C_{\mathrm{tu}} - \frac{N}{2}(C_{\mathrm{Ag}} - [\mathrm{Ag}^+]) \tag{6}$$

3. Results and discussion

In the initial approach, formation of only mononuclear Agtu_n complexes was considered. This approach, however, did not yield credible results. First, calculated stability constants were strongly dependant on concentration of Ag^+. For example, calculated $\log \beta_{11}$ in $\mathrm{HClO_4}$ solutions varied from 5.15 at $C_{\mathrm{Ag}} = 0.0001$ M to 8.48 at $C_{\mathrm{Ag}} = 0.001$ M, and to 10.28 at $C_{\mathrm{Ag}} = 0.01$ M. In some cases iterative calculations failed to converge.

Second, upon introduction of small amounts of thiourea (so that $C_{\mathrm{tu}} < C_{\mathrm{Ag}}$) to the system, the concentration of Ag^+ ions varied not according to the mononuclear model. Addition of thiourea (equal to 50% of the initial C_{Ag}) reduced the concentration of free Ag^+ ions by 70–75%, unexpected if only mononuclear complexes were formed; the maximum drop of concentration of Ag^+ ions would be equal to the amount of thiourea added, corresponding to formation of 1 : 1 complex. Higher than expected drop in $C_{\mathrm{Ag+}}$ clearly indicated that a complex with excess Ag was forming. According to literature, the most likely structure of such complex is $\mathrm{Ag_2tu}$ [6].

Third, earlier reports suggested formation of complexes $\mathrm{Ag_2tu_3}$ [12] and $\mathrm{Ag_2tu_6}$ [5, 19]. Assuming that $\mathrm{Ag_2tu}$, $\mathrm{Ag_2tu_3}$ and $\mathrm{Ag_2tu_6}$ are formed, it did seem reasonable to expect that the other three binuclear complexes would also be formed since the bonding in all complexes is similar.

Considering these facts, we attempted to calculate complex stability constants assuming that binuclear Ag^+ complexes $\mathrm{Ag_2tu}_n$ were forming. Calculated stability constants for all systems studied are presented in table 1. At lower concentration of silver ions ($C_{\mathrm{Ag}} = 0.001$ M) the determination and identification of larger complexes was unsuccessful since they likely were formed only to a small extent. In contrast to the former approach, calculated complex stability constants were not dependant on concentration of Ag^+ and were similar for all acids studied (table 2). For perchloric acid, the results were in a relatively good agreement with literature data and fitted well experimental data (example given in figure 1). Literature reports suggest that Ag coordination number is four in isolated solid-state Ag–tu complexes and, if required, the fourth site is filled with counterion [15, 16, 19, 20]. Considering that the structure of complexes formed was little affected by the acidity and type of acid used, free sites were, most likely, filled with $\mathrm{H_2O}$ since acid anions used in this study were bulky. Based on available literature data [16, 19] schematic representation of $\mathrm{Ag_2tu}_n$ complexes was proposed (figure 2). Ag atoms were in the center of distorted coordination tetrahedra, whereas two sulfur atoms acted as bridging ligands in a four-membered Ag–S–Ag–S ring. Upon addition of thiourea to the solution, $\mathrm{H_2O}$ was gradually replaced with tu [9], explaining the smooth drop of potential upon titration.

Table 1. Calculated stability constants of binuclear complexes Ag_2tu_n.

Acid used	C_{Ag}	log β21	log β22	log β23	log β24	log β25	log β26
$HClO_4$	0.0001	9.65	16.75	20.95	26.60		
	0.001	9.60	16.70	21.20	26.30	28.54	30.20
	0.01	9.12	16.31	21.40	26.90	29.09	30.35
HSO_3CH_3	0.0001	9.35	15.80	20.49	25.90		
	0.001	9.80	16.45	21.40	25.70	27.65	29.53
	0.01	9.20	16.13	21.40	27.45	28.66	30.66
HSO_3NH_2	0.0001	9.70	15.25	20.50	23.14	25.90	
	0.001	9.50	15.50	21.30	23.76	26.30	28.07
	0.01	9.38	16.18	21.05	23.82	26.10	

Table 2. Calculated average stability constants of binuclear complexes Ag_2tu_i in various acids and comparison with literature data.

	$SO_3CH_3^-$	$SO_3NH_2^-$	ClO_4^-	Literature data for ClO_4^-
Log β21	9.4 ± 0.4	9.5 ± 0.2	9.5 ± 0.3	9.3 [14], 9.1 [6]
Log β22	16.1 ± 0.3	16.0 ± 0.4	16.6 ± 0.3	17.0 [14], 16.1 [6]
Log β23	20.8 ± 0.4	20.9 ± 0.2	21.2 ± 0.2	22.6 [14], 21.7 [6]
Log β24	26.4 ± 0.2	23.6 ± 0.4	26.6 ± 0.4	25.7 [14]
Log β25	28.2 ± 0.6	26.2 ± 0.2	28.6 ± 0.4	27.0 [14]
Log β26	29.9 ± 0.4	28.1 ± 0.2	30.3 ± 0.2	31.1 [5]

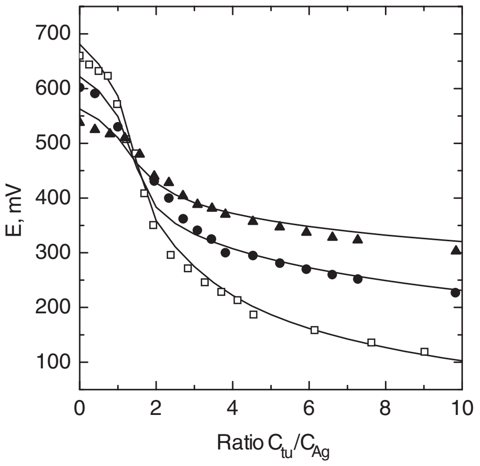

Figure 1. Potentiometric titration of Ag solutions with tu in 1 M HSO_3NH_2 acid solutions. Ionic strength 1.5 M. Symbols represent experimental points, straight line represents computational results. Concentration of silver ions C_{Ag}: ▲ –0.0001M, ● –0.001 M, □ –0.01 M.

In the third step the presence of both mononuclear and binuclear silver complexes was considered. This approach failed since the number of constants (10) was too high to fit results credibly and calculated stability constants varied too much.

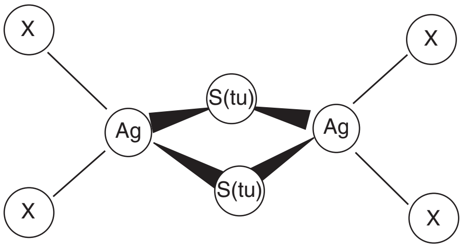

Figure 2. Schematic structure of Ag_2tu_n ($n = 2$ to 6) complexes. Depending on complex stoichiometry X represents either thiourea or water.

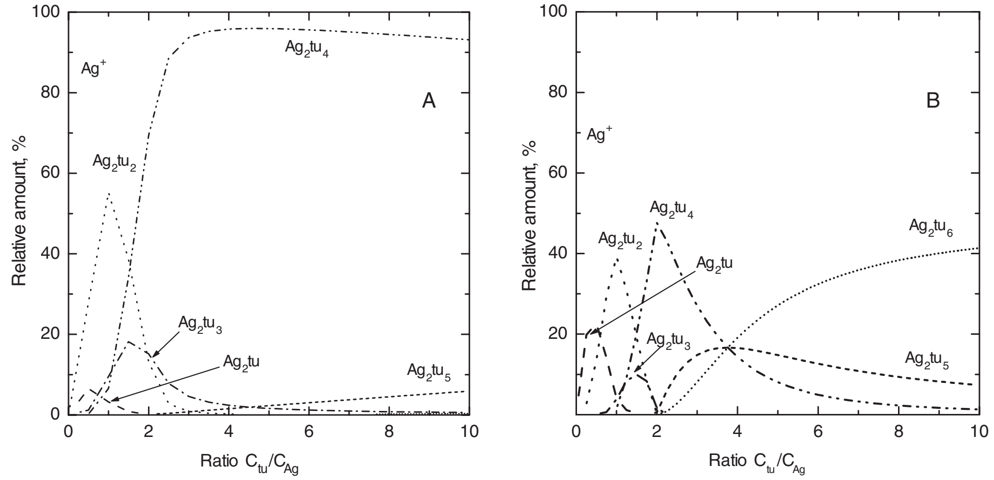

Figure 3. Calculated distribution of binuclear Ag_2tu_i complexes in HSO_3CH_3 acid solutions. (A) $C_{Ag} = 0.0001$ M; (B) $C_{Ag} = 0.01$ M.

Although we could not exclude the possibility that some mononuclear silver complexes were formed, especially at lower C_{Ag}, we could not identify them reliably. This is different from earlier reports claiming that mononuclear complexes are formed predominantly. Several possible reasons could be given to explain this discrepancy. Lower concentration of silver, lower ionic strength, and different method of computation could all be the reason for this disagreement.

In our study we could not find any polymeric complexes, though literature indicates such a possibility since the degree of agglomeration depends on the concentration of silver ions [12b]. For example, silver forms highly aggregated complexes with thiourea in dimethyl sulfoxide [15] and solid complexes with ratios 1 : 1 and 1 : 2 (Ag : tu) are polymeric [16, 20]. Those complexes, however, were obtained either in solid state or at very high concentrations of silver (≥ 1 M); the suggested threshold for formation of polymeric complexes (0.025 M) is higher than concentrations used in this work. The presence of primarily binuclear complexes in this concentration interval (C_{Ag} varied from 10^{-4} to 10^{-2} M), thus, seemed reasonable.

The calculated distribution of complexes indicates that even at low ratios of C_{tu}/C_{Ag} (≤ 1) several complexes are present in the solution simultaneously (example figure 3).

Thus computational approaches, based on assumption that at any given ratio it is possible to single out one dominating complex, are incorrect. At higher ratios of C_{tu}/C_{Ag} (≥ 5) dominant complex depends strongly on the concentration of Ag(I). At C_{Ag+} concentrations higher than 0.001 M Ag_2tu_6 dominated, whereas at lowest studied concentration ($C_{Ag} = 0.0001$ M) complex Ag_2tu_4 was the most important. Those observations were consistent with the fact that no stability constants of Ag_2tu_5 and Ag_2tu_6 were determined in systems with lowest content of Ag. Also, complexes with even numbers of thiourea ligands and with two bridging thioureas were more stable and dominating. It is not surprising since Ag(I) is known to form complexes with higher coordination numbers with "class b" ligands, such as those bonding through sulfur [15, 21].

4. Conclusions

Experimental and literature data indicate that complex formation between Ag and thiourea is very complex and strongly affected by many factors. It was established that under conditions similar to the ones used for commercial electroplating, silver and thiourea form predominantly binuclear complexes Ag_2tu_n ($n = 1$–6). Calculated complex stability constants indicate that the acidity and type of acid used have little effect on the structure of complexes. Ag ions in complexes were likely four-coordinate with additional sites filled with solvent molecules. Upon introduction of thiourea water molecules were replaced, forming a labile equilibrium mixture where a number of complexes were present simultaneously.

Although Ag–thiourea complexes appear to be promising candidates for Ag electroplating, slow decomposition of thiourea in acid and possible formation of polymeric precipitates could become hurdles that are hard to overcome. The use of thiourea derivatives could be beneficial since they are more stable and less likely to form polymeric chains. Additional research is necessary.

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