

## Article

# Investigating the Suitability of Various Silver(I) Complexes for Use in a Cyanide-Free Silver Electrolyte

Christoph Baumer , Udo Schmidt and Andreas Bund 

Electrochemistry and Electroplating Group, Technische Universität Ilmenau, 98693 Ilmenau, Germany; udo.schmidt@tu-ilmenau.de (U.S.); andreas.bund@tu-ilmenau.de (A.B.)

\* Correspondence: christoph.baumer@tu-ilmenau.de

**Abstract:** The suitability of various nitrogen, sulfur, oxygen, and phosphorus compounds as complexing agents in a silver electrolyte was examined by using potentiometric titration under practical conditions. The setup consisted of three electrodes to measure the pH and the activity of the silver ions simultaneously. Different ratios of silver to complexing agent from 1:10 to 1:1 at a constant ionic strength of 0.2 mol/L were investigated. The type of the complexes and their corresponding critical stability constants were evaluated by fitting the measured data using a self-developed algorithm. The pH and Nernst potential curve were calculated for the assumed complexes based on the law of mass action to find the best approximation. The correct definition of the occurring species is challenging and can lead to significant changes in the calculation of stability constants. For this reason, the measured silver potential curves were primarily used for the rating of the complexing agents. An evaluation of the measurements shows that the donor atom of the complexing agent and its ligand field strongly affected the stability and type of the complexes. Only a few complexing agents were found to be suitable for use in the cyanide-free silver electrolyte.

**Keywords:** silver; electroplating; cyanide-free; potentiometric titration; complexing agent



**Citation:** Baumer, C.; Schmidt, U.; Bund, A. Investigating the Suitability of Various Silver(I) Complexes for Use in a Cyanide-Free Silver Electrolyte. *Coatings* **2024**, *14*, 618. <https://doi.org/10.3390/coatings14050618>

Academic Editor: Eduardo Guzmán

Received: 12 April 2024

Revised: 7 May 2024

Accepted: 9 May 2024

Published: 14 May 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Silver is widely used in electroplating because it has the highest electrical conductivity and a lower price than other precious metals. It is possible to deposit silver from acid or alkaline electrolytes. Because of the location of the Nernst potential and the better throwing power, the deposition of silver from complexes in alkaline electrolytes is the most commonly used electroplating process. As a complexing agent, cyanide is used almost exclusively because of the high process stability, excellent layer properties, and process costs it offers [1]. But cyanide electrolytes pose a significant potential risk due to the formation of hydrogen cyanide. For reasons relating to safety and environmental protection, cyanide should be replaced by non-toxic and ecologically compatible complexing agents [2]. There is already a large number of studies on this subject, but only a few complexing agents have made it into industrial applications [3]. These are primarily succinimide [3–5], hydantoin derivatives [6,7], and, to a small extent, thiosulfate [8], as well as some other complexing agents [9,10]. However, cyanide-free electrolytes are not comparable to cyanide-based electrolytes in all their properties. Especially noteworthy is that there is no commercial electrolyte for the deposition of layers thicker than 50  $\mu\text{m}$  [1,11].

The development of a cyanide-free electrolyte for this application requires suitable complexing agents for silver. Therefore, in this study, a screening of various possible compounds was carried out under practical conditions. Hereby, a strong complexation of the silver ions is very important because it is a decisive factor for the morphology and quality of the layer. Furthermore, deposition on less noble metals (e.g., copper, nickel) is only possible if the concentration of the free silver ions is sufficiently low. This also prevents the formation of silver hydroxide in strongly alkaline solutions. Further criteria for our

selection of the studied compounds were the toxicity of the chemicals, their price, their availability, and ecological aspects.

The silver ion mostly forms linear complexes with two ligand molecules due to its electron configuration [12,13]. In such a complex, there are  $\sigma$ -bonds between the silver ions and the donor atom of the ligand. The strength of the bonds depends on the donor atom and its ligand field [14]. But the behavior and strength of the complex cannot be easily predicted or calculated. In particular, there is a lack of data on complexing and reaction behavior with silver for complexing agents that are often used in electroplating. That is why this study investigates the complexation of silver(I) ions via nitrogen, sulfur, oxygen, or phosphorus atoms and complexing agents of different structures. Due to the pH dependence of the complexation of silver ions, the complexing agents can be examined using potentiometric titration. This method combines acid–base titration, as used in Bjerrum methods [15], with a simultaneous measurement of the silver activity to determine the structure and stability constant of the complexes. By adding the base, the concentration of the deprotonated complexing agent increases, and the formation of the complex begins. With the decreasing activity of the silver ions, the silver potential decreases according to the Nernst equation (Equation (3)). Under the condition of an almost constant ionic strength, the activity of the silver ions is proportional to their concentration, which is used for the calculations of the critical stability constants.

Our simultaneous measurement of the pH value and the silver concentration and the self-developed algorithm for the evaluation of both measurement curves represent the merits of this work. Furthermore, different ratios of the silver to the complexing agent were examined to observe and better distinguish the differences in the species that formed. A total of 29 readily available and environmentally friendly substances were examined; their stability constants with silver were determined, and from these, suitable complexing agents were identified. This is an important step for the development of a cyanide-free silver electrolyte.

## 2. Experimentation

### 2.1. Methods and Materials

The titrations were carried out using an automatic titrator, namely Titrand 809 from Metrohm. For the pH measurement, a combined glass electrode SenTix H from WTW (Xylem Analytics, Weilheim, Germany) was used. The Nernst potential was measured with a silver ion-selective electrode (Ag-ISE) OP-Ag-0711P from Radelkis (Budapest, Hungary) vs. a saturated silver/silver chloride electrode (SSSCE). The reference electrode was connected to the analyte solution via a salt bridge containing 1 mol/L potassium nitrate to slow down the diffusional transport of chloride ions.

For the investigation of the complexing agents, different ratios of silver to ligand from 1:10 to 1:1 were measured. For this purpose, the silver concentration varied from 1 mmol/L to 10 mmol/L using reagent-grade silver nitrate 0.1 mol/L ampoules from Arzneimittelwerk Dresden (Dresden, Germany) with a purity of 99%. The concentration of the complexing agents was always 10 mmol/L. Most of the complexing agents were commercial products. Only uracil-1-acetic acid was prepared through the reaction of uracil and chloroacetic acid [16]. The sources and purity levels of the complexing agents are listed in Table A1 in Appendix A. All titrations were performed at a high ionic strength of 0.2 mol/L by using potassium nitrate (VEB Jenapharm, Jena, Germany, purest grade).

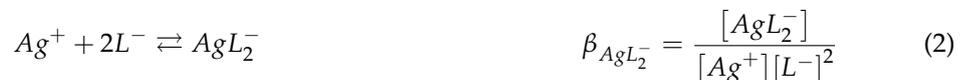
For the titration, a volume of 100 mL was used. The measurements were performed under constant stirring with a magnetic stirrer at  $22.0 \pm 1$  °C. The analyte was first adjusted to pH 2 with nitric acid 1 mol/L (nitric acid 65% reagent, Ph Eur, Merck KGaA, Darmstadt, Germany). The actual measurement was carried out via titration to pH 12 by adding potassium hydroxide 0.2 mol/L (potassium hydroxide flakes  $\geq 85\%$ , Merck KGaA, Darmstadt, Germany). The titrant solutions were prepared using a balance with a precision of 0.1 mg. The titer of the solutions was determined using commercial standard solutions (0.1 mol/L hydrochloric acid, Riedel-de Haën, Seelze, Germany) and was considered in

the subsequent evaluations. The measurement process was completely automated using the software tiamo™ 3.0 by Metrohm (Filderstadt, Germany). This software performs an intelligent titration, where the added volume is controlled according to the changing rate of the pH value. Each measurement consisted of 70–100 points in the range of pH 2 to pH 12 depending on the equivalence points during the titration.

For the calibration of the pH electrode, four buffers from Radiometer Analytical (Hach Lange, Düsseldorf, Germany) with pH levels of 1.679, 4.005, 7.000, and 10.012 were used. The determined slopes were between 55.6 and 57.0 mV/pH (=95.0%–97.4%) and the zero points were between pH 6.8 and 7.0 ( $R^2 > 99.9\%$ ). Calibration of the Ag-ISE was performed by measuring the potential in solutions with different silver concentrations. According to the Nernst equation (Equation (3)), the plot of the measured potential against the initial concentration of the silver ions should have a slope of 58.6 mV per decade and the y-intercept should correspond to the difference between the standard electrode potentials of Ag/Ag<sup>+</sup> (799 mV [17]) and the potential of the SSSCE (200 mV [18]). The determined slopes were between 56 and 59 mV per decade and the intersect was between 208 and 212 mV, which is caused by a systematic deviation of the potential of the SSSCE. The quality of the Ag-ISE potential measurement can also be extracted from the potentiometric titration for complexing agents that do not complex the silver ions in strong acids (starting pH of 2).

## 2.2. Mathematical Description

The stability of a complex of silver (Ag) and a ligand (L) is described by the law of mass action according to the formation reaction of the complex. For the most common complexes, i.e., AgL and AgL<sub>2</sub><sup>−</sup>, the stability constants  $\beta_{AgL}$  and  $\beta_{AgL_2^-}$  are given by Equations (1) and (2) [15]:



A high critical stability constant is not the decisive factor for the development of a silver electrolyte. The crucial element is the concentration of the free silver ions because this determines the equilibrium potential of the silver deposition and dissolution according to the Nernst equation (Equation (3)). A deposition on copper or nickel is only possible if the Nernst potential is sufficiently low.



The concentration of the free silver ions depends on the type of complex and the concentration of the ligand molecules bound to the silver ion. There must be a lone pair of electrons on the donor atom, which is why in most cases a proton must be removed from the ligand. The complexation therefore also depends on the activity of the protons. The concentration of deprotonated complexing agents is also described by the mass of law action, depending on the number of protons that can be donated. The acid dissociation constants ( $K_1$  and  $K_2$ ) for a dibasic ligand are given by Equations (4) and (5):



Some of the examined complexing agents can form protonated complexes in which the ligand is not completely deprotonated. In the simplest case, the according critical stability constant  $\beta$  is defined by Equation (6) [19,20]:



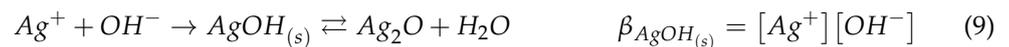
A generalized description of the stability constant obtained from Equations (1), (2) and (4)–(6) is given by Equation (7):



The following relationship (Equation (8)) applies to the acid–base constants ( $a = 0, c = 1$ ):

$$\beta_{Ag_aH_bL_c}(a = 0, c = 1) = \beta_{H_bL} = \sum_b K_b \quad (8)$$

Titration can also lead to the formation of insoluble species that precipitate from the electrolyte. Silver tends to form insoluble silver hydroxide in strongly alkaline solutions. This subsequently reacts to form silver oxide ( $Ag_2O$ ) with the elimination of water. The solubility limit is described by the solubility constant ( $\beta_{AgOH(s)}$ ), as seen in Equation (9):



### 2.3. Evaluation of the Measurements

Our measurements were evaluated by simulating the pH and silver potential curves using a self-developed algorithm. The concentration  $c_1$  of the silver ions, the fully protonated complexing agent, and the protons can be calculated by solving a system of nonlinear equations (Equations (10)–(13)). The nonlinearity of these mass balances arises due to the definitions of the equilibrium constants in Equations (1), (2) and (4)–(9), where the concentrations of the reactants appear with their stoichiometric factors in the exponent. The number of terms in the mass balances corresponds to the number of species ( $j$ ) that appear during the titration. These must be defined before the evaluation. Our notation is based on the freeware Hyperquad Simulation and Speciation (HySS2009) [21,22], in which the species are defined in the form of a table. In this table, the header row defines a generic species formula of type  $Ag_aH_bL_c$ , with  $a$ ,  $b$ , and  $c$  being the stoichiometric factors of the silver, protons, and ligands, respectively. Using this notation, in the following rows, the occurring species and corresponding equilibrium constant are listed (Table 1).

**Table 1.** Definition of the species for creating the mass balances (Equations (10) and (11)) based on the freeware HySS2009 [22], using succinimide as an example.

	Species Formula	Silver Ag <sup>+</sup>	Protons H <sup>+</sup>	Ligands L <sup>-</sup>	Log Constant (Equilibrium)
	Ag <sub>a</sub> H <sub>b</sub> L <sub>c</sub>	a	b	c	β <sub>j</sub>
Complexes	AgL	1	0	1	β <sub>1</sub>
	AgL <sub>2</sub> <sup>-</sup>	1	0	2	β <sub>2</sub>
Protonated complexing agent	HL	0	1	1	β <sub>3</sub>
Solids/precipitations	AgOH	1	-1	0	β <sub>4</sub>

This structure allows the programming of loops that go through each row and create single terms for each species in the mass balances (Equations (10)–(13)). In this notation, hydroxylated species are defined by a negative stoichiometric factor, denoted as  $b$ . The

concentration of the hydroxide ions is calculated through the autoprotolysis constant of water ( $K_w = 10^{13.77}$ ), like in Equation (13) [23]. For the insoluble products, the apparent concentration is calculated by dividing their mass by the titration volume [21,24]. These concentrations must be added in the mass balances as an additional variable (Equation (15)). The initial concentrations for silver  $[Ag^+]_0$  and the complexing agent  $[L]_0$ , as well as the added volume  $V_{KOH}$  and concentration  $c_{KOH}$  of the titrant (KOH), are entered into the equations as constants. It should be noted that the titration volume increases during the titration. This dilution must be considered when calculating each individual titration volume.

$$f_1(c_i) = [Ag^+] + \sum_j a_j \beta_j [Ag^+]^{a_j} [H^+]^{b_j} [L^-]^{c_j} + [AgOH_{(s)}] - [Ag^+]_0 \quad (10)$$

$$f_2(c_i) = [L^-] + \sum_j a_j \beta_j [Ag^+]^{a_j} [H^+]^{b_j} [L^-]^{c_j} - [L]_0 \quad (11)$$

$$f_3(c_i) = [H^+] + \sum_j a_j \beta_j [Ag^+]^{a_j} [H^+]^{b_j} [L^-]^{c_j} + \beta_{AgOH_{(s)}} \cdot \frac{10^{13.77}}{[AgOH_{(s)}]} - [H]_0 + V_{KOH} c_{KOH} \quad (12)$$

$$f_4(c_i) = \beta_{AgOH_{(s)}} \cdot \frac{10^{13.77}}{[H^+]} - [AgOH_{(s)}] \quad (13)$$

This system of nonlinear equations is solved using Newton's method [25]. The functions  $f_i(c_i)$  are combined into a vector  $\overrightarrow{F(I)}$  (Equation (14)) that must be minimized by finding the concentrations for each variable  $c_i$ . For this purpose, the Jacobi matrix (14) with first-order partial derivatives is calculated from the system of equations. The first derivative can again be easily calculated by iterating through Table 1.

$$\overrightarrow{c_{i,n}} = \begin{pmatrix} [Ag^+]_n \\ [L^-]_n \\ [H^+]_n \\ [AgOH \downarrow]_n \end{pmatrix} \quad \overline{J(c_{i,n})} = \begin{pmatrix} \frac{\partial f_1(c_{i,n})}{\partial [Ag^+]} & \frac{\partial f_1(c_{i,n})}{\partial [L^-]} & \frac{\partial f_1(c_{i,n})}{\partial [H^+]} & \frac{\partial f_1(c_{i,n})}{\partial [AgOH \downarrow]} \\ \frac{\partial f_2(c_{i,n})}{\partial [Ag^+]} & \frac{\partial f_2(c_{i,n})}{\partial [L^-]} & \frac{\partial f_2(c_{i,n})}{\partial [H^+]} & \frac{\partial f_2(c_{i,n})}{\partial [AgOH \downarrow]} \\ \frac{\partial f_3(c_{i,n})}{\partial [Ag^+]} & \frac{\partial f_3(c_{i,n})}{\partial [L^-]} & \frac{\partial f_3(c_{i,n})}{\partial [H^+]} & \frac{\partial f_3(c_{i,n})}{\partial [AgOH \downarrow]} \\ \frac{\partial f_4(c_{i,n})}{\partial [Ag^+]} & \frac{\partial f_4(c_{i,n})}{\partial [L^-]} & \frac{\partial f_4(c_{i,n})}{\partial [H^+]} & \frac{\partial f_4(c_{i,n})}{\partial [AgOH \downarrow]} \end{pmatrix} \quad (14)$$

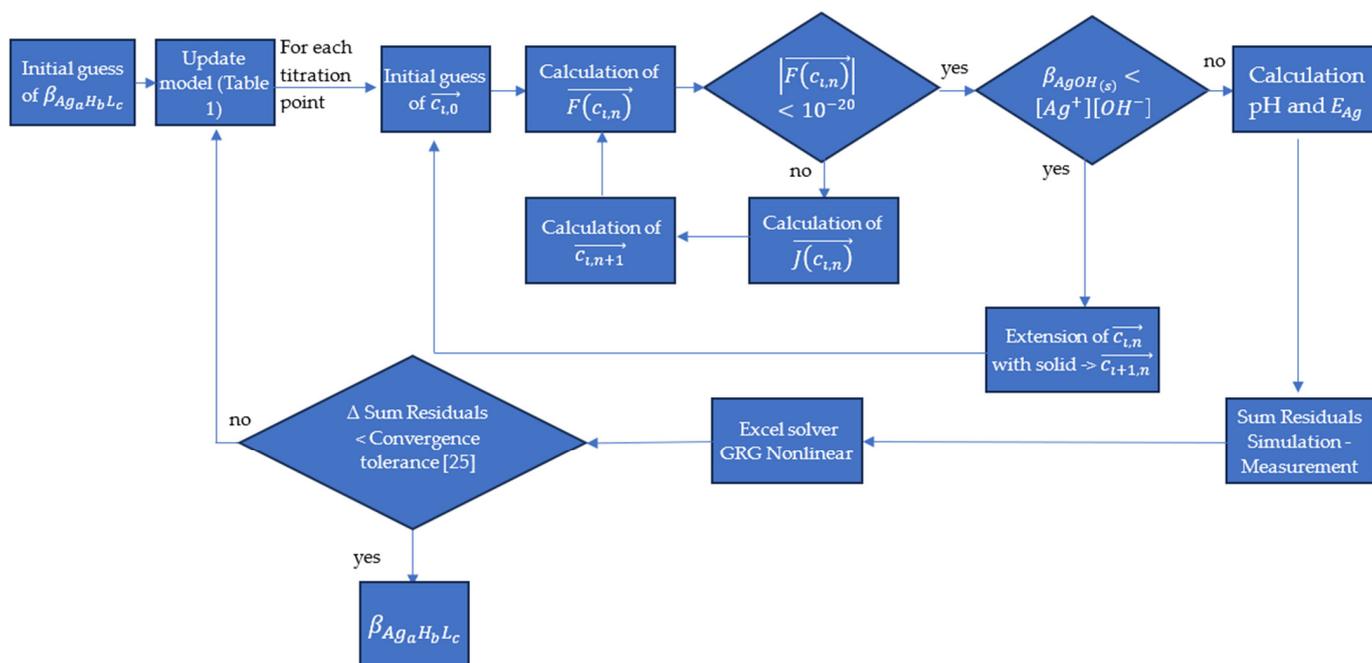
According to Newton's method, a new set of variables is calculated in each iteration until the vector  $\overrightarrow{F(I_{i,n})}$  has reached a minimum:

$$\overrightarrow{c_{i,n+1}} = \overrightarrow{c_{i,n}} - \lambda \cdot \overline{J(c_{i,n})}^{-1} \times \overrightarrow{F(c_{i,n})} \quad (15)$$

To increase the stability of the algorithm, a damping factor  $\lambda$  is used to prevent large changes in the variables. The algorithm only allows the variable to be changed by a maximum of 50%. The system of nonlinear equations must be solved for every point/volume of the titration. In the case that no insoluble species occur, the matrix equations are reduced by one dimension. Both cases must be calculated one after the other in this algorithm because the structure of the matrix equations changes (Figure 1).

After solving the system of nonlinear equations, the concentrations of all other species ( $Ag_a H_b L_c$ ) can be calculated for each point of the titration depending on the specified equilibrium constants (Table 1). This allows the simulation of the pH value and Nernst potential during the titration. These values can then be compared with the measured values at each point of the titration to obtain the sum of all squares of deviations. With the Excel solver, this deviation can be minimized by varying the equilibrium constants to achieve the greatest agreement between the simulation and measurement results. The advantage

of replicating HySS2009 (version 4.0.31, Protonic software, Eastbourne, UK) in Excel and Visual Basic (Microsoft 365 MSO, version 2403, Redmond, WA, USA) is that it offers the possibility to simultaneously evaluate the pH and Nernst potential measurement. Therefore, the calculations of the equilibrium constants are based on an extended dataset. Furthermore, the silver potential curve supports the interpretation of the processes during the titration and the complexes. The correct definition of the occurring species is the greatest challenge in evaluating these measurements. However, this programming method is flexible enough that several metals, complexing agents, and insoluble species can be simulated. The measurements and evaluation meet the minimum requirements for equilibrium data as described by Martell et al. [23].



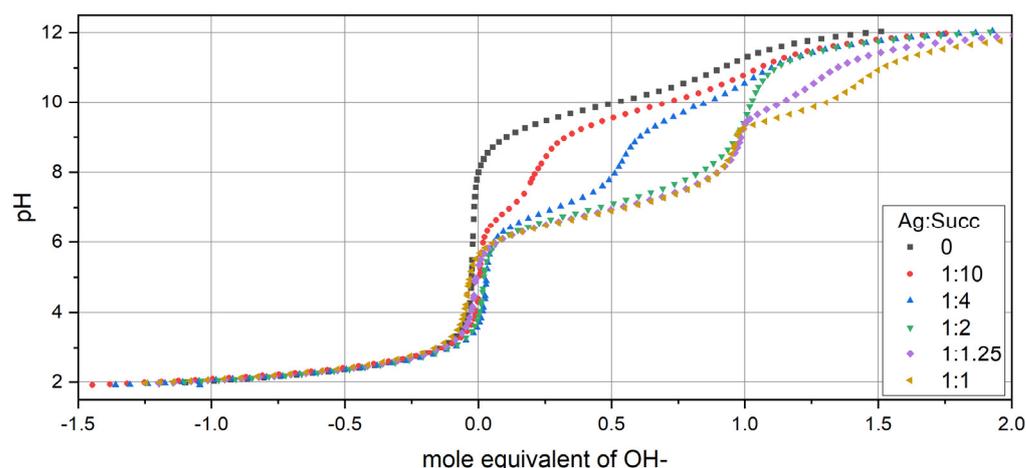
**Figure 1.** Stepwise logic of the self-developed algorithm for the evaluation of the measured pH and silver potential curves for the determination of the equilibrium constants [26].

### 3. Results

#### 3.1. Potentiometric Titration of Succinimide (Succ)

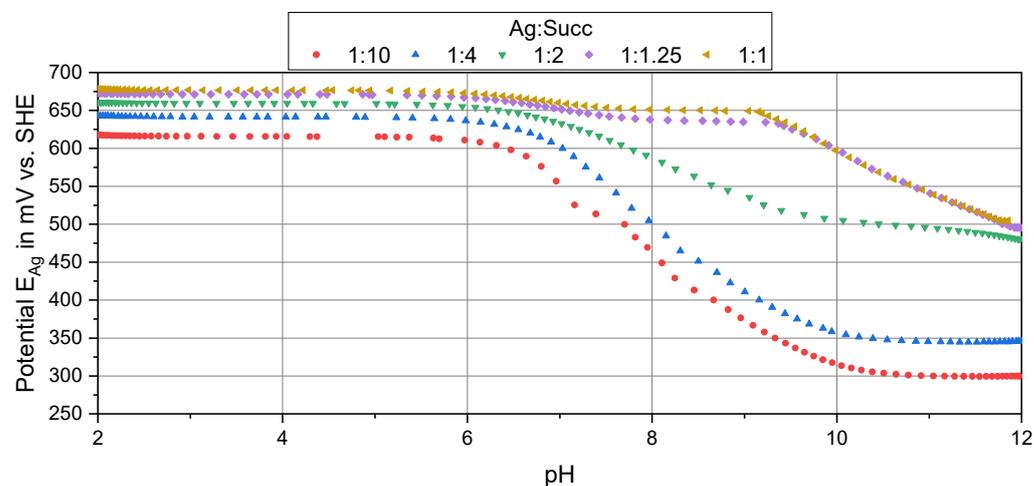
One of the first complexing agents for non-cyanide silver electrolytes was succinimide, which is evaluated below to explain the evaluation of the potentiometric measurements. Succinimide is a monobasic acid and forms  $\text{AgL}$  and  $\text{AgL}_2$  complexes with silver ions depending on the ratio of silver to succinimide (Table 1). Five different ratios, as well as the pure complexing agent, were examined. The analyte of 10 mmol/L succinimide without silver shows an equivalence point at a zero mole equivalent of  $\text{OH}^-$  and can be used as a reference for the evaluation of the analytes of silver and succinimide (Figure 2).

These curves also have an equivalence point at a zero mole equivalent, but the shift in pH is significantly smaller. Between pH 6.5 and 7.5, there is an additional consumption of the added hydroxide, because of the formation of silver complexes, which releases protons. The second equivalence point shifts to higher mole equivalents as the ratio between silver and succinimide increases. The mole equivalents are equal to twice the amount of the initial silver concentration. Accordingly, at this point, the formation of the  $\text{AgL}_2$  complex is complete. If the ratio of silver to succinimide becomes larger than 1:2, complete complexation of the silver ions is not possible. The precipitation of silver hydroxide starts at pH 9, which becomes visible through a rapid black color change of the analyte due to the subsequent formation of silver oxide. As soon as all of the uncomplexed silver has precipitated as silver hydroxide, a third pH jump occurs.



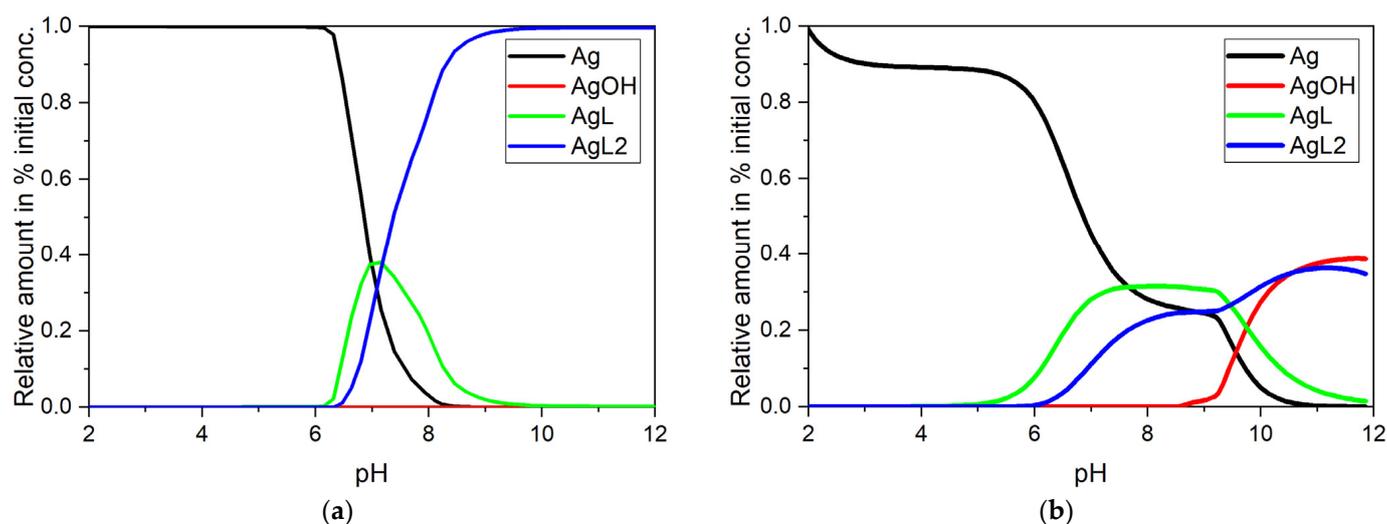
**Figure 2.** PH curves of potentiometric titration using different ratios of silver to succinimide. Analytes contained 0–10 mmol/L silver nitrate, 10 mmol/L succinimide, and 0.2 mol/L potassium nitrate.

As described above (Section 2.1), no complexation of silver ions by succinimide occurs in the acidic pH range (Figure 3). The potentials at pH 2 correspond to the initial concentrations of silver nitrates. Starting at pH 6.5, the potential drops significantly, and the complexation of the silver ions begins. For the analytes with an excess of the complexing agent, the potential drops to 300–350 mV vs. SHE at pH 10. This potential drop is directly proportional to the stability of the silver complexes. Without excess, at a ratio of silver to succinimide of 1:2, the potential only drops to around 480 mV vs. SHE. If the complexation is insufficient (ratios 1:1.25 and 1:1), the precipitation of silver hydroxide starts at pH 9. The potential of the Ag-ISE decreases linearly with the pH.



**Figure 3.** Silver potential vs. SHE for potentiometric titration using different ratios of silver to succinimide. Analytes contained 1–10 mmol/L silver nitrate, 10 mmol/L succinimide, and 0.2 mol/L potassium nitrate.

By calculating all of the species occurring during the potentiometric titration, a species distribution diagram can be created (Figure 4). This chart contains the relative amount of each species in relation to the initial concentrations depending on the pH value. For a ratio of silver to succinimide of 1:10, there is only a significant amount of the  $\text{AgL}$  complex in the pH range of 5 to 8. The  $\text{AgL}_2$  complex is the dominant silver species above pH 7 (Figure 4a).



**Figure 4.** Calculated species distribution during the potentiometric titration of the following analytes: (a) 1 mmol/L silver nitrate, 10 mmol/L succinimide, and 0.2 mol/L potassium nitrate; (b) 10 mmol/L silver nitrate, 10 mmol/L succinimide, and 0.2 mol/L potassium nitrate.

In comparison, the AgL complex is present at significantly higher pH values at a ratio of 1:1. The occurrence of the AgL<sub>2</sub> complex is significantly reduced at this ratio due to the limited amount of succinimide. At high pH values, only the AgL<sub>2</sub> complex and the precipitated silver hydroxide are present (Figure 4b). Accordingly, the AgL complex only has a small influence on the shape of the measured curves at silver-to-succinimide ratios < 1:2. This is the reason why the stability constant of the AgL complex cannot be determined with certainty at these ratios. At higher ratios, determination is possible. Likewise, the solubility product of silver hydroxide can only be determined at ratios > 1:2 since precipitation only occurs at these ratios. The equilibrium constants that can be determined with certainty were calculated in this study for each ratio between silver and succinimide (Table 2). The averaged values are in accordance with other results reported in the literature [23], although any deviations are partly due to the different ionic strengths and temperatures used during the potentiometric titration.

**Table 2.** Calculated equilibrium constants for the complexing agent succinimide depending on the silver-to-ligand ratio, and a comparison of these values with other published values [23].

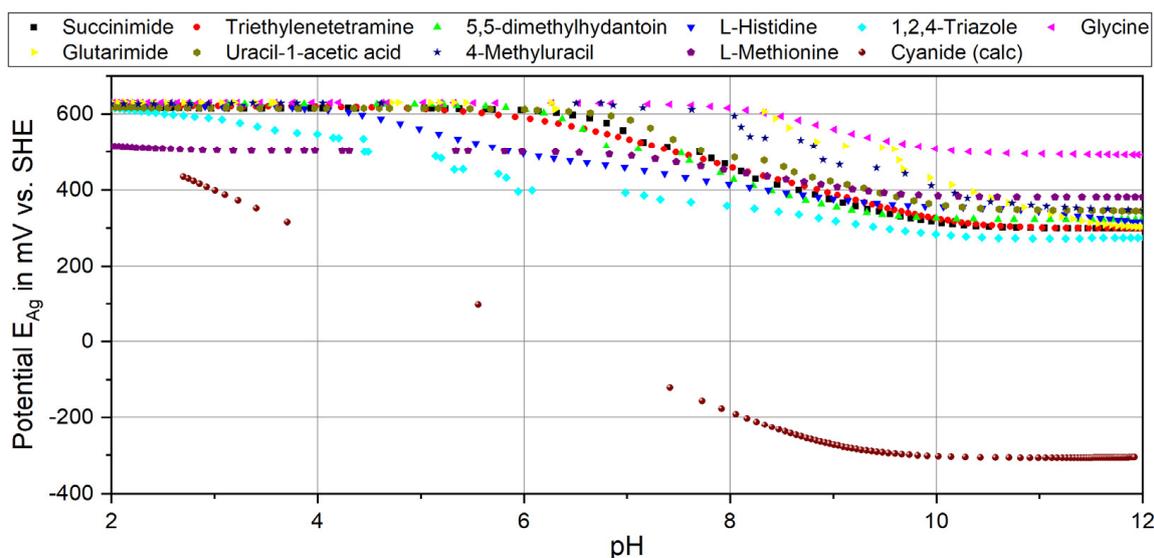
Equilibrium Constant	Ratio of Silver to Succinimide (Ag/L)						Average	Standard Deviation	Published Values [23]
	0	1:10	1:4	1:2	1:1.25	1:1			
$\lg\beta_{\text{AgL}}$		5.3	4.6	5.2	5.0	5.0	5.0	0.25	5.2
$\lg\beta_{\text{AgL}_2^-}$		9.7	9.8	9.9	10.1	10.1	9.9	0.17	9.6
$\lg\beta_{\text{HL}}$	9.9	9.5	9.4	9.8	9.7	9.8	9.7	0.22	9.54
$\beta_{\text{AgOH}_{(s)}}$				7.5	7.3	7.3	7.4	0.08	7.8

### 3.2. Evaluation of the Studied Complexing Agents

#### 3.2.1. Nitrogen Compounds

Analogous to succinimide, 28 further complexing agents for silver were examined via potentiometric titration. An evaluation of their equilibrium constants was conducted by averaging the measurements of three to eight different silver-to-ligand ratios (Table A2). The largest group of complexing agents examined were nitrogen compounds, as some of these substances are already used in commercial electrolytes [3–5]. Most of these compounds behave similarly. They are weak acids that complex the silver ions after deprotonation. Therefore, the silver potential started to decrease during the measurements between

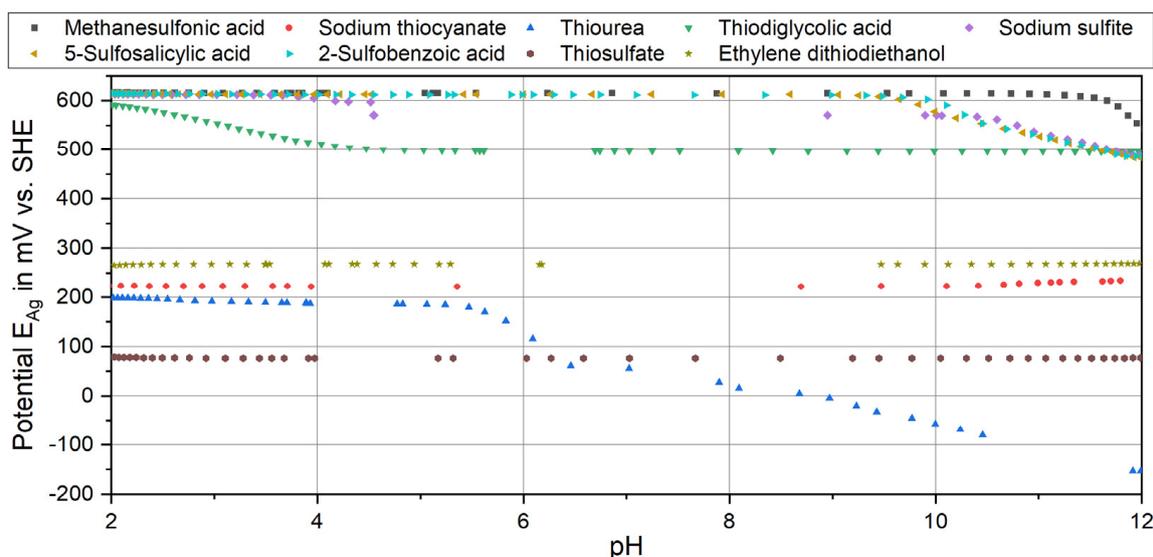
pH 6 and 7 (Figure 5). For a silver-to-ligand ratio of 1:10, the potential reached its minimum at pH 10, with values around 300 mV vs. SHE. Glycine is a weaker complexing agent for silver, with stability constants of 3.7 for the AgL complex and 6.3 for the AgL<sub>2</sub> complex. The minimum silver potential is 500 mV vs. SHE at pH 10. 1,2,4-Triazole formed an insoluble white precipitation at the beginning of the titration. Furthermore, it is noticeable that during the titration of L-methionine and L-histidine, the potential decreased well before pH 6 was reached, because these compounds formed AgHL complexes with the silver. Nevertheless, the reached potentials are significantly higher than the potential that can be reached with cyanide, the almost exclusively used complexing agent for industrial silver plating.



**Figure 5.** Silver potential curves against SHE for the studied nitrogen compounds at a silver-to-ligand ratio of 1:10 (1 mmol/L silver nitrate, 10 mmol/L complexing agent, 0.2 mol/L potassium nitrate). The values for cyanide are calculated from data reported in the literature.

### 3.2.2. Sulfur Compounds

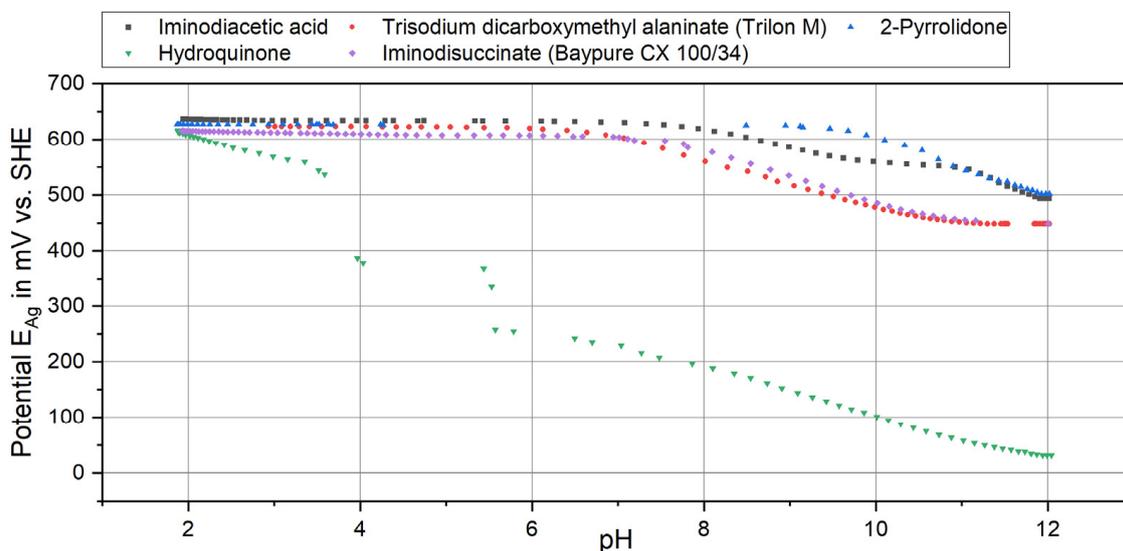
The studied sulfur compounds displayed a less homogeneous behavior. Methanesulfonic acid, 5-sulfosalicylic acid, 2-sulfobenzoic acid, and sulfite showed no complexation of the silver ions during the measurements (Table A2). The silver potential was constant up to a pH value of 10 and then only precipitated due to the formation of silver hydroxide (Figure 6). Thiocyanate, thiodiglycolic acid, thiourea, and thiosulfate formed an insoluble precipitate with silver, which already occurred during the preparation of the analyte. This could be clearly seen through the formation of brown and partly flake-shaped precipitates before starting the titration. Because of the low solubility constants, the concentrations of the free silver ions are extremely low, which resulted in a very low silver potential. The solubility constant for the precipitation with thiodiglycolic acid appears to be higher because the silver potential does not become as negative. However, these substances cannot be used as complexing agents for a silver electrolyte. Only ethylene dithiodiethanol could be a suitable complexing agent for the silver electrolyte, especially because it forms strong AgHL complexes. This complexing agent is a commercial product of TIB Chemicals.



**Figure 6.** Silver potential curves against SHE for the studied sulfur compounds at a silver-to-ligand ratio of 1:10 (1 mmol/L silver nitrate, 10 mmol/L complexing agent, 0.2 mol/L potassium nitrate).

### 3.2.3. Oxygen Compounds

In this study, five oxygen compounds were tested. 2-Pyrrolidone showed no complexation (Table A2). Iminodiacetic acid is a weak complexing agent and could not prevent the formation of silver hydroxide at higher pH values (Figure 7). Trisodium dicarboxymethyl alaninate ( $\text{Na}_3\text{MGDA}$ ) and iminodisuccinate formed more stable complexes, with stability constants around 5 for the  $\text{AgL}$  complex. Hydroquinone behaved similarly to the sulfur compounds described above and formed an almost insoluble compound with silver, meaning it cannot be used for a commercial electrolyte.

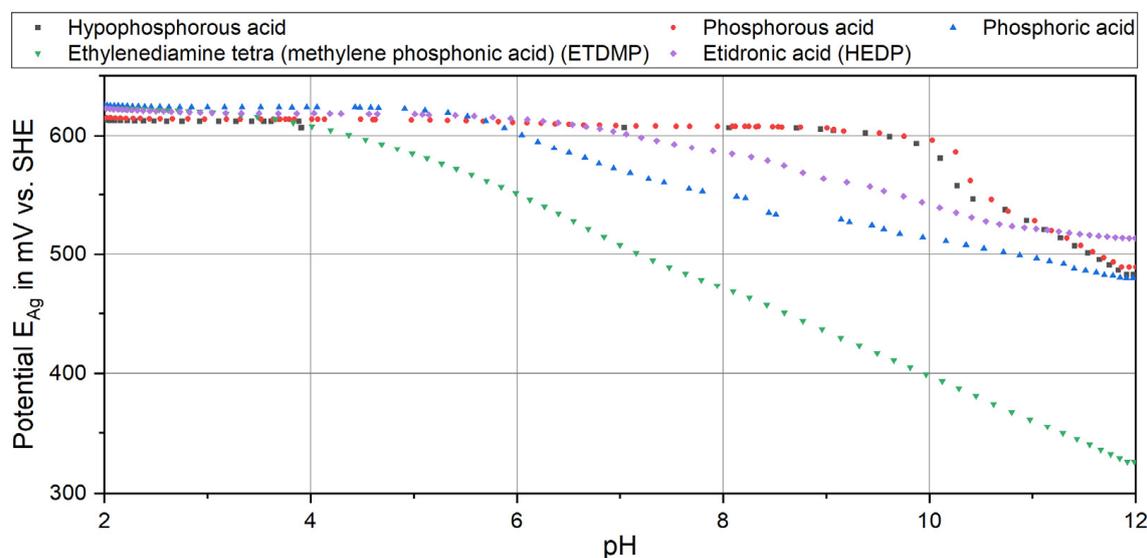


**Figure 7.** Silver potential curves against SHE for the studied oxygen compounds at a silver-to-ligand ratio of 1:10 (1 mmol/L silver nitrate, 10 mmol/L complexing agent, 0.2 mol/L potassium nitrate).

### 3.2.4. Phosphorous Compounds

Apart from ethylenediamine tetra(methylene phosphonic acid) (EDTMP), the studied phosphorus compounds are not or are only weak complexing agents, which did not prevent the formation of silver hydroxide at higher pH values (Table A2). EDTMP complexed the silver ions sufficiently. However, this complex was also at most moderately strong, with a

stability constant of 5 for the  $\text{AgL}$  and 10 for the  $\text{AgL}_2$  complex. The early decrease in silver potential at pH 3.5 was caused by the formation of  $\text{AgHL}$  complexes (Figure 8).



**Figure 8.** Silver potential curves against SHE for the studied phosphorous compounds at a silver-to-ligand ratio of 1:10 (1 mmol/L silver nitrate, 10 mmol/L complexing agent, 0.2 mol/L potassium nitrate).

#### 4. Discussion

The hypothesis that the stability and type of occurring complexes depends on the donor atom of the complexing agent was generally confirmed. The results show that most of the nitrogen compounds examined are moderately strong complexing agents for silver. The sulfur compounds often show the formation of insoluble precipitates due to the high affinity of silver for sulfur. Phosphorous and oxygen compounds are mostly weak complexing agents. The aim of this study was to search for new complexing agents for a cyanide-free silver electrolyte. Of the 29 studied complexing agents, several are suitable for further investigation. These are succinimide, 5,5-dimethylhydantoin, L-methionine, triethylenetetramine, L-histidine, uracil-1-acetic acid, glutarimide, and EDTMP. These complexing agents lead to a sufficiently strong complexation to enable deposition on copper (337 mV vs. SHE [17]). But none of these complexing agents can be used for direct electroplating on nickel because of its negative Nernst potential (−250 mV vs. SHE [17]). Furthermore, these complexing agents prevent the precipitation of silver hydroxide at higher pH values. Succinimide and 5,5-dimethylhydantoin are compounds that are already used in commercial products. The others have so far hardly been investigated regarding their use in cyanide-free silver electrolytes. In particular, the compounds that form  $\text{AgHL}$  complexes would have an advantage for such electrolytes, because a larger working pH range could be possible. With ethylene dithiodiethanol, silver deposition from an acidic electrolyte would be possible. The other complexing agents can only be used at high pH values  $\geq 10$ , otherwise there is insufficient complexation of the silver ions.

The calculated stability constants are in approximate agreement with the tabulated or published values, as far as these are available. The differences can be partly explained by the different measurement methods and conditions, such as the concentration of silver, the complexing agents, the ionic strength, and the temperature. For succinimides, the differences in the determined constants are in the range of 0.2–0.4 and thus in the range of two standard deviations (Table 2). Thereby, the determined standard deviations of the measurements are comparatively high compared to other studies [19,23]. In accordance with the aim of this study to investigate the occurring species, the same measurements were not repeated, but rather different ratios of silver to complexing agent were measured. These

calculations were further influenced by uncertainties in the definition of the occurring species. In the first attempt, the linear complexes  $\text{AgL}$  and  $\text{AgL}_2$ , which mainly occur in silver, were used. For more complex systems, information was taken from the latest research in the literature. It should also be mentioned that in some cases, substances of technical purity were used, as only these are suitable for technical electrolytes. Any impurities can influence the course of the measured curves. An example of this can be seen with triethylenetetramine.

The next step for the development of a cyanide-free electrolyte would be to investigate the electrochemical deposition of silver out of electrolytes containing the new complexing agent. For industrial applications, the silver concentration should be in the range of 10–50 g/L (0.1–0.5 mol/L) to achieve a sufficient deposition rate. The concentration of the complexing agent must be at least two times higher. This can be concluded from the experiments because otherwise the formation of  $\text{AgL}_2$  complexes is not complete. To achieve stable conditions and a low silver potential, a 3–5-fold excess of the complexing agent in relation to the silver should be chosen (Figure 3). It must be investigated whether sufficient solubility and stability of the complexes and complexing agents can be achieved under these conditions. In future studies, the mechanism of silver deposition and the quality of the electroplated layers from the new electrolytes must be tested. These investigations will probably reduce the number of suitable complexing agents.

## 5. Conclusions

This work describes the search and investigation for new complexing agents for environmentally friendly, non-toxic silver electrolytes. For this purpose, 29 different nitrogen, sulfur, oxygen, and phosphorus compounds were examined by using potentiometric titration. The pH and the potential of the free silver ions were simultaneously measured. An evaluation of the measurements was conducted based on Bjerrum's method. Thereby, we created our own algorithm to determine the complexes and stability constants (Table A2). From our measurements, it can be concluded that the complexation of silver ions strongly depends on the donor atom and ligand field of the complexing agent. Overall, nitrogen compounds are very promising for use as complexing agents in a cyanide-free electrolyte. Among the sulfur, oxygen, and phosphorous compounds studied here, only a few substances are suitable. Direct electroplating on nickel would not be possible with any of these studied complexing agents.

**Author Contributions:** Conceptualization, funding acquisition, supervision, resources, writing—review and editing: A.B.; methodology, writing—review and editing: U.S.; software, validation, formal analysis, investigation, data curation, writing—original draft preparation, visualization, project administration: C.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Federal Ministry for Economic Affairs and Climate Action (BMWK) on the basis of a decision made by the German Bundestag, grant number KK5112708JN1. The APC was funded by the Open Access Publication Fund of the Technische Universität Ilmenau.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The raw data supporting the conclusions of this article and the Visual Basic code and Excel worksheet will be made available by the authors on request.

**Acknowledgments:** The authors thank Adriana Ispas and Violeta-Tincuta Gruia for initiating this project, as well as Michael Stich and Christine Gießler for proofreading the article. The authors also thank TIB Chemicals AG for providing the complexing agent ethylene dithiodiethanol.

**Conflicts of Interest:** The authors declare no conflicts of interest. The funders had no role in the design of this study; in the collection, analyses, or interpretation of the data; in the writing of the manuscript; or in the decision to publish the results.

## Appendix A

**Table A1.** List of the substances examined as complexing agents, each described with the IUPAC name, supplier, and purity used.

Substance	IUPAC Name	Supplier	Purity
Succinimide	Pyrrolidine-2,5-dione	VEB Jenapharm, Jena, Germany	98%
Glycine	Aminoacetic acid	Reanal, Budapest, Hungary	98%, <0.2% sulph. Ash <0.05% NH <sub>3</sub>
5,5-dimethylhydantoin	4,4-Dimethyl-2,5-dioxoimidazolidin	Sigma-Aldrich, Merck KGaA, Darmstadt, Germany	97%
Ethylenediamine tetra (methylene phosphonic acid) (ETDMP)	{Ethane-1,2-diylbis[nitrilobis(methylene)]}-tetrakis(phosphonic acid)	Zschimmer & Schwarz, Lahnstein, Germany	94.7%, 0.03% Cl <sup>-</sup>
Etidronic acid (HEDP)	1-Hydroxyethylidene-1,1-diphosphonic acid	Zschimmer & Schwarz, Lahnstein, Germany	83.8% 0.06% H <sub>3</sub> PO <sub>3</sub> 0.01% Cl <sup>-</sup>
Iminodiacetic acid	2,2'-Azanediyldiacetic acid	Fluka, Fisher Scientific GmbH, Schwerte, Germany	90%, ~10% H <sub>2</sub> O
L-Histidine	L-2-Amino-3-(1H-imidazol-4-yl)propanoic acid	Reanal, Budapest, Hungary	98.5%
L-Methionine	L-2-amino-4-(methylthio)butanoic acid	VEB-Berlin-Chemie, Berlin, Germany	99%
Triethylenetetramine	N1,N1'-(Ethane-1,2-diyl)di(ethane-1,2-diamine)	Arcos Organics, Schwerte, Germany	60% tech.
Thiodiglycolic acid	2-(carboxymethylsulfanyl)acetic acid	Thermo-Fisher, Darmstadt, Germany	98%
Uracil-1-acetic acid	3,4-Dihydro-2,4-dioxo-1(2H)-pyrimidineacetic acid	Prepared [16]	98%
Trisodium dicarboxymethyl alaninate (Trilon M)	Trisodium;2-[bis(carboxylatomethyl)amino]propanoate	BASF, Ludwigshafen, Germany	40%
Iminodisuccinate (Baypure CX 100/34)	Tetrasodium N-(1,2-dicarboxylatoethyl)- $\xi$ -aspartate(2-)	Lanxess, Köln, Germany	34%
Sodium sulfite	Sodium sulfite	Reanal, Budapest, Hungary	p.A.
Thiourea	Thio urea	Binnenhandel Herzberg, Herzberg, Germany	p.A.
Sodium thiocyanate	Sodium thiocyanate	VEB Berlin-Chemie, Berlin, Germany	p.A.
5-Sulfosalicylic acid	2-Hydroxy-5-sulfobenzoic acid	VEB Berlin-Chemie, Berlin, Germany	p.A.
Phosphoric acid	Phosphoric acid	VEB Jenapharm, Jena, Germany	99%
Phosphorous acid	Phosphonic acid	Riedel-de Haën, Seelze, Germany	>98%
Hypophosphorous acid	Phosphinic acid	Fluka, Fisher Scientific GmbH, Schwerte, Germany	48.0–52.0%
Methanesulfonic acid	Methanesulfonic acid	Carl Roth, Karlsruhe, Germany	≥99%
2-Sulfobenzoic acid	2-sulfobenzoic acid	VEB Laborchemie, Apolda, Germany	p.A.

Table A1. Cont.

Substance	IUPAC Name	Supplier	Purity
2-Pyrrolidone	Pyrrolidin-2-one	Sigma Aldrich, Merck KGaA, Darmstadt, Germany	≥99%
Glutarimide	Piperidine-2,6-dione	Sigma Aldrich, Merck KGaA, Darmstadt, Germany	98%
Thiosulfate	Thiosulfate	Reanal, Budapest, Hungary	p.A.
Hydroquinone	Benzene-1,4-diol	Reanal, Budapest, Hungary	p.A.
1,2,4-Triazole	1H-1,2,4-Triazole	Carl Roth, Karlsruhe, Germany	≥98%
4-Methyluracil	6-methyl-1H-pyrimidine-2,4-dione	Reanal, Budapest, Hungary	p.A.
Ethylene dithiodiethanol (TIB Suract ETG)	2-[2-(2-hydroxyethyl)disulfanyl]ethyl)ethanol	TIB Chemicals, Mannheim, Germany	technical grade

## Appendix B

Table A2. Summary of the determined equilibrium constants and standard deviations for the studied complexing agents.

Complexing Agent	Probable Donor Atom	pK <sub>a</sub>	Number of Titrations	Complex	log β <sub>Ag<sub>a</sub>H<sub>b</sub>L<sub>c</sub></sub>	SD log β <sub>Ag<sub>a</sub>H<sub>b</sub>L<sub>c</sub></sub>
Succinimide	N	9.7	6	AgL	5	0.25
				AgL <sub>2</sub>	9.7	0.17
Glycine	N	2.1	9	AgL	3.7	0.24
		9.4		AgL <sub>2</sub>	6.3	0.27
5,5-dimethylhydantoin	N	8.9	9	AgL	4.9	0.33
				AgL <sub>2</sub>	9.2	0.47
Ethylenediamine tetra (methylene phosphonic acid) (ETDMP)	P	2.3	9	AgH <sub>3</sub> L	27.7	0.20
		3.5		AgH <sub>2</sub> L	22.2	0.32
		5.5		AgHL	13.8	0.59
		6.5		AgL	6.9	0.63
		8.0				
Etidronic acid (HEDP)	P	<2	9	AgL	2.6	0.41
		2.9		AgL <sub>2</sub>	5.5	1.40
		7.5				
Iminodiacetic acid	O	2.7	9	AgL	3.7	0.05
		9.5				
L-Histidine	N	2.1	9	AgHL	13	0.33
		6.1		Ag(HL) <sub>2</sub>	23.8	0.88
		9.1		Ag <sub>2</sub> L <sub>2</sub>	16.4	0.43
L-Methionine	N/S	2.7	9	AgH <sub>2</sub> L	15.6	0.05
		9.2		AgHL	13.2	0.10
				AgL	6.1	0.06
				AgL <sub>2</sub>	7.9	0.17
Triethylenetetramine	N	3.7	9	AgL	7.4	0.12
		6.7		AgL <sub>2</sub>	9.8	0.06
		7.8				
		9.8				
Thiodiglycolic acid	S	4.2 7.5	4			Insoluble precipitate

Table A2. Cont.

Complexing Agent	Probable Donor Atom	pK <sub>a</sub>	Number of Titrations	Complex	log β <sub>Ag<sub>a</sub>H<sub>b</sub>L<sub>c</sub></sub>	SD log β <sub>Ag<sub>a</sub>H<sub>b</sub>L<sub>c</sub></sub>
Uracil-1-acetic acid	N	9.7	4	AgL	5.0	0.27
				AgL <sub>2</sub>	9.2	0.38
Trisodium dicarboxymethyl alaninate (Trilon M)	O	<2	4	AgL	5.1	0.16
		2.6				
		10.2				
Iminodisuccinate (Baypure CX 100/34)	O	3.3	4	AgL	4.5	0.30
		3.5				
		4.7				
		10.3				
Sodium sulfite	O	1.8 6.9	4	No complexation detected		
Thiourea	S	<2	4	Insoluble precipitate		
Thiosulfate	S	<2	4	Insoluble precipitate		
Sodium thiocyanate	S	<2	4	Insoluble precipitate		
5-Sulfosalicylic acid	O	<2	4	No complexation detected		
Phosphoric acid	P	2.1	2	AgHL	15.7	0.28
		6.8		AgL	5.5	0.21
		12.3				
Phosphorous acid	P	2.2 6.7 >12	2	No complexation detected		
Hypophosphorous acid	P	<2	2	No complexation detected		
Methanesulfonic acid	S	<2	4	No complexation detected		
2-Sulfobenzoic acid	O	<2	4	No complexation detected		
Hydroquinone	O	10.2 11.6	3	Insoluble precipitate		
2-Pyrrolidone	N	>12	4	No complexation detected		
Glutarimide	N	11.5	4	AgL	5.1	0.12
				AgL <sub>2</sub>	10.5	0.50
1,2,4-Triazole	N	2.5	4	Insoluble precipitate		
4-Methyluracil	N	9.5	4	AgL	4.7	0.85
				AgL <sub>2</sub>	9.2	0.69
Ethylene dithiodiethanol (TIB Suract ETG)	S	>12	4	Ag(HL) <sub>2</sub>	38.2	3.29

## References

1. Yli-Pentti, A. 4.11—Electroplating and Electroless Plating. In *Comprehensive Materials Processing*; Hashmi, S., Batalha, G.F., Van Tyne, C.J., Yilbas, B., Eds.; Elsevier: Oxford, UK, 2014; pp. 277–306, ISBN 978-0-08-096533-8.
2. Satpathy, B.; Jena, S.; Das, S.; Das, K. A comprehensive review of various non-cyanide electroplating baths for the production of silver and gold coatings. *Int. Mater. Rev.* **2023**, *68*, 825–861. [[CrossRef](#)]
3. Berger, S.; Hoffacker, G. Novel and innovative non-cyanide silver process: A report on commercial plating experiences. *Plat. Surf. Finish.* **2005**, *92*, 46–51.
4. Gan, H.; Liu, G.; Huang, C.; Tang, R.; Liu, Y.; Shi, C. The influence of pH and current density for nano-silver electrodeposited in cyanide-free succinimide bath. *Surf. Interfaces* **2021**, *27*, 101487. [[CrossRef](#)]
5. Dini, J.W.; Morrissey, R.J.; Pacheco, D.R. Materials characterization of a non-cyanide silver electrodeposit. *Plat. Surf. Finish.* **1997**, *84*, 62–67.

6. Liu, A.; Ren, X.; Wang, B.; Zhang, J.; Yang, P.; Zhang, J.; An, M. Complexing agent study via computational chemistry for environmentally friendly silver electrodeposition and the application of a silver deposit. *RSC Adv.* **2014**, *4*, 40930–40940. [CrossRef]
7. Liu, A.; Ren, X.; Wang, C.; Zhang, J.; Du, C.; Han, R.; An, M. DMH and NA-based cyanide-free silver electroplating bath: A promising alternative to cyanide ones in microelectronics. *Ionics* **2021**, *27*, 417–422. [CrossRef]
8. Ren, F.; Yin, L.; Wang, S.; Volinsky, A.A.; Tian, B. Cyanide-free silver electroplating process in thiosulfate bath and microstructure analysis of Ag coatings. *Trans. Nonferrous Met. Soc. China* **2013**, *23*, 3822–3828. [CrossRef]
9. Jasni, A.B.; Yoshihara, S.; Aiki, F.; Watanabe, H. Pyrimidine derivative-based cyanide-free silver electroplating bath. *Trans. IMF* **2022**, *100*, 193–199. [CrossRef]
10. Xie, B.-G.; Sun, J.-J.; Lin, Z.-B.; Chen, G.-N. Electrodeposition of Mirror-Bright Silver in Cyanide-Free Bath Containing Uracil as Complexing Agent Without a Separate Strike Plating Process. *J. Electrochem. Soc.* **2009**, *156*, D79. [CrossRef]
11. Cai, H.; Li, Y.; Wu, Y.; Zhang, H.; Zhang, Y.; Sun, Y.; Wang, G.; Song, J.; Ding, G. Non-Cyanide Thick Silver Electrodeposition Base on Instantaneous Nucleation for 3D Microstructures with High Performance. *J. Electrochem. Soc.* **2023**, *170*, 22504. [CrossRef]
12. Fox, B.S.; Beyer, M.K.; Bondybey, V.E. Coordination chemistry of silver cations. *J. Am. Chem. Soc.* **2002**, *124*, 13613–13623. [CrossRef] [PubMed]
13. Schwarzenbach, G.; Anderegg, G. Über die Stabilität großer Chelatringe. *Z. Anorg. Allg. Chem.* **1955**, *282*, 286–292. [CrossRef]
14. Nguyen, L.H.; Tran, D.P.; Truong, T.N. Computational Study on the Nature of Bonding between Silver Ions and Nitrogen Ligands. *ACS Omega* **2022**, *7*, 45231–45238. [CrossRef] [PubMed]
15. Bjerrum, J. On the tendency of the metal ions toward complex formation. *Chem. Rev.* **1950**, *46*, 381–401. [CrossRef] [PubMed]
16. Shvachkin, Y.P.; Azarova, M.T. Potential antimetabolites. IV. Derivatives of 3-uracilylacetic acid. *Zh. Obshch. Khim.* **1963**, *33*, 590.
17. de Bethune, A.J.; Licht, T.S.; Swendeman, N. The Temperature Coefficients of Electrode Potentials. *J. Electrochem. Soc.* **1959**, *106*, 616. [CrossRef]
18. Haider, C. *Electrodes in Potentiometry*; Metrohm Ltd.: Herisau, Switzerland, 2004.
19. Bottari, E.; D'Ambrosio, A.; Festa, M.R.; Iuliano, M.; Meschino, M.; de Tommaso, G. Stability and Structure of Silver–l-methionine Complexes. *J. Solut. Chem.* **2022**, *51*, 1393–1408. [CrossRef]
20. Martell, A.E.; Motekaitis, R.J. *The Determination and Use of Stability Constants*, 2nd ed.; VCH: Weinheim, Germany, 1992; ISBN 3527895167.
21. Alderighi, L.; Gans, P.; Ienco, A.; Peters, D.; Sabatini, A.; Vacca, A. Hyperquad simulation and speciation (HySS): A utility program for the investigation of equilibria involving soluble and partially soluble species. *Coord. Chem. Rev.* **1999**, *184*, 311–318. [CrossRef]
22. Gans, P.; Sabatini, A.; Vacca, A. HySS Hyperquad Simulation and Speciation. Available online: <http://www.hyperquad.co.uk/hyss.htm> (accessed on 10 April 2024).
23. Martell, A.E.; Smith, R.M.; Motekaitis, R.J. NIST Standard Reference Database 46 Version 8.0: NIST Critically Selected Stability Constants of Metal Complexes. 2004. Available online: <https://www.nist.gov/srd/nist46> (accessed on 5 April 2024).
24. Ingri, N.; Kakolowicz, W.; Sillén, L.G.; Warnqvist, B. High-speed computers as a supplement to graphical methods—V11Part IV—Arkiv Kemi, **1964**, *23*, 97; for comments on spelling “program” see *Talanta*, **1967**, *14*, 833.; Haltafall, a general program for calculating the composition of equilibrium mixtures. *Talanta* **1967**, *14*, 1261–1286. [CrossRef] [PubMed]
25. Sebah, P.; Gourdon, X. Newton’s method and high order iterations. *Numbers Comput.* **2001**, *1*, 1–10.
26. Microsoft. SolverOptions Function. Available online: <https://learn.microsoft.com/en-us/office/vba/excel/concepts/functions/solveroptions-function> (accessed on 5 April 2024).

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.