Reactive Precipitation of Silver Powders

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ABSTRACT

The present research project is part of an overall study whose aim is to develop a process for the production of silver powders by the reduction of silver nitrate with hydrazine. This is an extremely fast reaction, which results in uncontrolled particle properties. The main objective was to develop conditions at which the rate of the reaction and hence the particle properties could be controlled; this was accomplished by carrying out the reaction under the presence of EDTA as a complexing agent. EDTA effectively slowed down the reaction still allowing it to take place at concentrations between 0.22 and 3.3 mM.

The analytical methods did not differentiate silver nanoparticles, which could not be filtered, from unreacted silver ions. Therefore, the reactive solutions were seeded so that crystal growth was favored over nucleation. A concentration of seeds of 0.27 mM was enough to avoid the production of nanoparticles. The silver reduction rate was found to be of order 1.1, 0.72 and –1.11 with respect to the silver, hydrazine and EDTA concentrations respectively. Silver crystal sizes were also evaluated at different conditions.

RÉSUMÉ

Les recherches présentes font partie d'une étude avec le but de développer un processus pour la production de poudres d'argent par la réduction de nitrate d'argent avec hydrazine. C'est une réaction extrêmement rapide, qui cause des propriétés de particule non contrôlées. L'objectif principal était de développer des conditions auxquelles le vitesse de la réaction et donc les propriétés des particules pourraient être contrôlées; c'a été accompli en effectuant la réaction dans la présence d'EDTA comme un agent complexant. EDTA a efficacement ralenti à la réaction lui permettant toujours d'avoir lieu aux concentrations entre 0.22 et 3.3 mM.

Les méthodes analytiques n'ont pas différencié argent nanoparticules, qui ne pouvait pas être filtré, d'ions non réagis d'argent. Donc, les solutions réactives ont été semées pour que la croissance de cristal ait été favorisée sur nucleation. Une concentration des graines de 0.27 mM était assez pour éviter la production de nanoparticules. La vitesse de réduction d'argent a été trouvé pour être de l'ordre 1.1, 0.72 et-1.11 en ce qui concerne les concentrations d'argent, hidrazine et EDTA respectivement. La taille des cristaux d'argent a aussi été évaluée dans des concentrations différentes.

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Table of Contents

List of Figures

List of Tables

CHAPTER 1. Introduction

1.1 General Overview

Silver powders are widely used in several applications of the electric and electronic industries. One of the most important is their role as the active part of conductive inks and pastes used in electronic components (Brady and Clauser, 1991). As the electronic and microelectronic industries have grown considerably during the last decades, the use of silver powders has increased accordingly.

The silver powders required by the industry must have high levels of purity. Also, it is desired to have powders which are homogeneous both regarding size and shape. However, this is specially difficult to achieve in terms of the size of the particles. The silver powders produced both industrially and in research laboratories are composed of particles of different sizes. Because of this, the particle size distribution is a critical characteristic for industrial purposes, being desirable narrow distributions for specific mean particle sizes.

There are several methods for the production of silver powders. These can be based on chemical, physical, electrochemical and thermal principles. One of the most popular methods is the precipitation of silver by the reduction of a silver salt. This process produces fine, narrowly distributed diameters for the silver particles, which is together with its low cost the reason for its wide use (Ducamp etc., 1992).

In the chemical precipitation of silver various reducing agents, both organic and inorganic, can be used. One of the most common is hydrazine (N_2H_4), which has been tested by several researchers for the reduction of silver salts (Jost, 1983; Qin, 1988; Cheng and Xia, 1996). Hydrazine presents several advantages, the main one being its high reducing potential. Also, a mole of hydrazine when oxidized completely can reduce up to four moles of silver salt. The salt commonly used for producing silver powders by reactive precipitation is the silver nitrate, though other salts can be as effective as this one.

The particle size distribution of the silver powder is a function of the process by which it was produced as well as the conditions under which this process was carried out. Therefore, for a certain method of production of silver powder, the adequate manipulation of the variables will potentially allow the production of particles with desired properties within certain parameters.

1.2 Statement of the Problem

In Chapter 2 previous work reported in the literature concerning the precipitation of silver particles by reduction of its salts will be discussed. In most of these, the aim has been the production of silver particles of small average diameters. The means to reach it were the use of different silver salts, reducing agents, or even chelating and protective agents. However, in all these studies there was not an attempt to control the rate of the reaction and the properties of the particles with the conditions prevailing in the reaction mixture.

For each industrial use of the silver powders, there is also a set of desired properties, mainly purity, mean particle size and particle size distribution. Due to this, a method by which silver powders of given properties can be produced by the manipulation of the operation variables is desired. In order to achieve this, a study related to the correlation between powder properties and the conditions at which they are manufactured is needed. Such study regarding the precipitation of silver has not been carried out.

Several mechanisms need to be looked at while studying the reactive crystallization of silver. Initially, the reduction takes place producing uncharged elemental silver atoms dissolved in the reactive solution. This elemental silver quickly generates a supersaturation which is the driving force that brings about the process of crystallization. Crystallization consists mainly of three steps: nucleation, growth and agglomeration of crystals. In addition to these steps, the breakage of crystals, also known as death, may also occur. The rates of nucleation and growth of the particles are functions of the conditions of the reaction mixture, such as reactant concentration, temperature and available surface area. These rates along with the agglomeration have a direct impact on the particle size distribution.

In order to produce particles of given properties, it is necessary either to develop a model or to carry out experiments in a trial and error procedure in order to set the operating conditions that will deliver the desired silver powders. Modeling has the advantage of being adaptable to predict the effect of modifications to the process. From this, the overall goal of this research project is to develop a model that predicts the properties of powder particles produced by reactive precipitation. The precipitation of silver powders with a given complexing agent is intended to be adapted to this model by the definition of parameters with experimental data.

The study presented in this Thesis is the first part of this broad research project. The first step to achieve is the study and characterization of the reduction of silver salts. Once the behavior of this reaction is well established, it will be possible to determine the properties of the particles produced, develop a model for reactive precipitation, and correlate the theoretical and experimental parts using the relevant parameters. Because of industrial interest, the reducing agent selected is hydrazine. However, the reaction of hydrazine with silver ions takes place at a very fast rate. In order to control the reduction rate, the effect of several complexing agents must be evaluated. Based on all this, the objectives of the present thesis were identified.

1.3 Objective

The main objective of the thesis is to study the reduction of silver salts with hydrazine for the precipitation of elemental silver. To achieve this, a complexing agent may be used so that the reaction is slow enough to be monitored experimentally. This goal can be subdivided into the specific objectives presented next.

- To evaluate the rate of reduction of silver with hydrazine modifying the reactant concentrations, pH value and temperature

- To determine the degree of oxidation of hydrazine, and therefore the stoichiometry of the silver – hydrazine reaction, under a variety of conditions

- To select and characterize an adequate complexing agent in order to slow down the silver reduction rate

- To evaluate the effect of hydrazine, silver, and the complexing agent concentrations on the rate of reduction

- To interpret the observed reduction rates as a result of the combination of the reaction and crystallization (i.e. nucleation, growth and agglomeration) rates

- To characterize the rate of reduction of silver with hydrazine under the effect of a given complexing agent as a function of the reactant concentrations

1.4 Outline of the thesis

The present thesis has been divided into six chapters. The contents of each chapter are briefly presented next.

- The first chapter, the Introduction, contains general information on the use and production of silver powders. Based on this information a statement of the problem to be treated is offered and finally the objectives are defined.

- In Chapter 2 a background on the production of silver powders by precipitation is offered. This chapter also explains the chemistry of hydrazine as a reducing agent and gives a basis on the equations of crystallization.

- Chapter 3 explains the materials and methods used for the experimental development of the thesis.

- Chapter 4 shows results of preliminary experiments carried out. The reduction of silver with hydrazine without a complexing agent is performed under several conditions and the use of a chelating agent is justified. Also in this chapter a determination of the stoichiometry of the silver – hydrazine reaction is carried out. Finally, experimental problems regarding the determination of hydrazine are displayed.

- Chapter 5 presents the core of the experimental results. In this chapter the complexing agent is selected and characterized. The effects of the concentrations in the observed rate of reaction are determined and explained. After this, an interpretation of the characteristic behavior observed is offered and proved experimentally. Finally, SEM pictures of the particles produced are shown and related to the experimental results and equations possibly very useful for the modeling are proposed.

- Chapter 6 summarizes the main conclusions achieved by the present work.

CHAPTER 2. Background

2.1 Crystallization and Precipitation

Crystallization is the conversion of a substance from an amorphous state, either solid, liquid or gas, to a crystalline state (Mersmann, 1995). This is one of the oldest unit operations in chemical engineering, being particularly important as a separation process for carrying substances from components of solutions or melts into their pure state. In order to achieve the steps of crystallization, the original phase at which the substance exists must be supersaturated. This level of supersaturation is the driving force of the crystallization. Based on the method to achieve supersaturation, crystallization can be classified into different categories, such as cooling, evaporation, drowning-out and reaction crystallization.

2.1.1 Precipitation, General Aspects

The term precipitation refers to nothing more than a fast crystallization, although in several occasions it also implies an irreversible process (Mullin, 1993). This way, many precipitates are insoluble or nearly insoluble substances while the crystals obtained from the classical methods of crystallization such as cooling and evaporation can be redissolved if the system is reverted to its original conditions. The silver powder production by the reduction of silver salts with hydrazine makes a perfect example of this process. Precipitation processes are generally initiated at high supersaturations, resulting in a fast nucleation and the consequent creation of large number of primary crystals. Thus, precipitation is a valuable alternative for the production of ultrafine powders (Söhnel et al., 1992).

In order to obtain the desired product quality in a crystallization process, it is of great importance to have an in-depth knowledge of the precipitation mechanism in order to design and control the precipitation reactor. Although several processes based on such knowledge have been successfully applied to conventional crystallization, the design of precipitation processes is still mostly based on experience, rather than on a scientific approach and modeling. The added complexity of precipitation modeling comes from the fact that precipitated crystals are formed from the competition of different processes, each one having its distinct kinetics. The complex interaction among chemical reaction, the different steps of crystallization (nucleation and growth) and mixing in the reactor, generally leads to a crystallization rate hard to control. Therefore, in order to control a precipitation process, it would be necessary to study the following competing events:

a) The kinetics of the chemical reactions, being the source of supersaturation
b) The kinetics of crystallization, including primary and secondary nucleation, crystal growth, agglomeration and Ostwald ripening, which is an important step in the precipitation of small particles (Klein and David, 1995)
c) The kinetics of mixing, including micromixing and macromixing

In order to understand the general behavior of a precipitation reactor, the different steps of crystallization must be identified and explained. In the following sections these steps will be briefly clarified.

2.1.2 Nucleation

When a solution is driven to supersaturation, the system tends to reach thermodynamic equilibrium through the formation and growth of nuclei. The formation of these nuclei is what we know as nucleation. Nucleation can be classified into primary nucleation, either homogeneous or heterogeneous, and secondary nucleation.

Primary nucleation is characterized by the formation of clusters in the absence of crystals in the solution, commonly known as seeds. In the case of homogeneous nucleation, the spontaneous and random fluctuations of density or composition result in the formation of small embryos. These embryos can be destroyed in the same way, unless they reach a critical size, becoming stable nuclei (Frenkel, 1955). In the case that foreign particles are present, nuclei are formed on the surface of these particles, bringing about the heterogeneous nucleation. Secondary nucleation, on the other hand, takes place when solution-own crystals are present, allowing the formation of new nuclei at very low supersaturation.

Mathematically, the rate of nucleation is defined as the change of the number of crystals per mass of solvent per unit time in the absence of agglomeration and breakage. This rate was described by Tavare and Garside (1986) by a general equation of the form:

$$B^\circ = dN / dt = k_N M_T^b S^C$$

where B° is the nucleation rate, N is the number of crystals per mass of solvent, k_N is the constant of nucleation, M_T is the magma density of the solution in kg of crystals per kg of solvent, S is the supersaturation level and b and c are independent parameters. In case that the nucleation is mainly secondary, the constant b is higher than zero. In case that the nucleation is primary, this is equal to zero. In recent years, a form of this equation taking into account the effect of the temperature was developed (Pinder and Mina-Mankarios, 1991; Pinder and Nyakiamo, 1996). The final equation taking all the effects into account is given by

$$B^\circ = k_N S^C M_T^b \exp(A_N/T)$$

where A_N is the activation energy for nucleation divided by the universal gas constant R.

2.1.3 Crystal Growth

The growth of crystals in a supersaturated solution is also a very complex process, in which several steps can be distinguished. These steps include the bulk diffusion, surface diffusion, desolvation, and integration into the lattice. Moreover, a variety of growth units (atoms, molecules, ions, clusters, etc.) exists depending on the crystallizing system and the solvent (Mersmann, 1995). This complexity has brought about the derivation of general equations that approximate the general behavior of the crystal growth.

Mathematically, crystal growth is defined as the change of the characteristic length of a crystal with respect to time. The general equation that describes the growth rate (Abegg et al., 1968) is given by

$$G = dL / dt = k_G \, S^d \, (1+L)^e$$

where L is the characteristic length of the crystal, k_G is the growth constant and d and e are equation parameters. In case the growth rate depends on the crystal size, e is different than zero; in case the growth rate is independent of the crystal length, e equals zero. This is a commonly used equation by several authors, however Smith and Sweett (1977) studied and used other growth rate expressions.

As in the case of the nucleation rate, there have been several studies for the growth rate with the purpose of incorporating the temperature into the growth rate equation (Pinder and Mina-Mankarios, 1991; Pinder and Nyakiamo, 1996). These have incorporated an Arrhenius type relationship to the growth rate equation, resulting in the following.

$$G = k_G \, S^d \, (1+L)^e \exp{(A_G/T)}$$

where A_G is the ratio of the growth activation energy and the universal gas constant.

2.1.4 Particle Agglomeration

Agglomeration is the process by means of which two particles collide and stick together to form a new, larger particle. Since it is one of the most important growth mechanisms in industrial applications, agglomeration increases the mean particle size, decreases the total particle concentration and does not affect the total crystal mass concentration. As the agglomeration reduces the total external surface area of the crystals, which corresponds to a net reduction in the Gibbs free energy at constant pressure and temperature, agglomeration is a thermodynamically favored process.

Agglomeration is a process driven by the collision of particles. Depending on the mechanism that causes the collision, it can be classified into three categories: perikinetic, orthokinetic and differential sedimentation aggregation. The frequency of collision of each category is governed by a different function.

The first case, perikinetic agglomeration, is an effect of Brownian motion. This kind of motion is the one observed for small particles in suspension, which undergo continuous random movements related to diffusion. The second case of agglomeration is the orthokinetic one. In general, aggregation processes are mostly carried out with the suspension being subjected to some form of shear, either by stirring or by flow. The collisions caused by this shear bring about what we know as the orthokinetic aggregation. One of the main differences between perikinetic and orthokinetic agglomeration rates is that in the second case there is a size dependant collision frequency, even for two particles of virtually the same size. Indeed, the collision frequency is proportional to the cube of the addition of the two radii, known as the collision radius. Because of this, as agglomeration proceeds and the aggregate size increases, the chance of collision becomes greater. In the perikinetic aggregation, on the other hand, even when for larger particles there is an increased collision radius, this is compensated by the lower diffusion coefficient of such larger particles.

In the case of orthokinetic agglomeration, the rate constant is greatly dependant on the particle size. This makes the analytical derivation of aggregate concentrations beyond very early stages of aggregation virtually impossible. However, it is possible, making assumptions about the form of aggregates, to carry out numerical computations of particle size distributions under orthokinetic conditions (Wiesner, 1992).

The third mechanism for particle agglomeration is the differential sedimentation. This phenomenon takes place when particles are sedimenting in a suspension. Larger particles sediment at a faster rate than smaller ones, and can capture the latter as they fall. The collision frequency can be calculated using the Stokes' law for the sedimentation rate of spherical particles (Friedlander, 1977). Differential settling is important mostly for large particles with a high density.

In the case of ultrafine powders in a well mixed reactor, it is expected that both the perikinetic and orthokinetic mechanisms will have an effect on agglomeration. On one hand, as the diameter of the particles produced is very small, their diffusion coefficient is large, promoting Brownian motion. On the other hand, having a well mixed reactor, particles are subjected to a strong shear resulting on orthokinetic agglomeration.

2.2 Chemical Reduction of Silver Salts

The suitability of powders for a certain industrial application is dictated by their properties. The properties of silver powders are strongly influenced by the particle size, shape and size distribution (Arai, 1996). Different methods of production will give powders of different properties. Therefore, in order to manufacture particles with desired size, shape and distribution, careful selection of the production technique is necessary. Many methods have been used for the production of silver powders. These include physical processes, like atomization and grinding, thermal decomposition, and finally chemical reduction of silver compounds and electrolytic deposition.

The chemical reduction of silver salts has been widely studied. This process can yield silver powders with the properties needed for the purposes of the electronics industry. Silver powders obtained by this method tend to have high purity, small size and a narrow particle size distribution. All these properties are desired to produce conductive silver pastes and inks.

The silver salt most widely studied is the silver nitrate, possibly because not many other silver salts are soluble (Greenwood, 1984). Even with the same silver salt the mean particle size of the produced silver powders depends strongly on the reducing agent used. Shaplygin (1970) tried hydrogen peroxide as the reducing agent producing particles with a mean diameter of 0.5 to 5 microns. Melashenko (1971) produced particles of 0.1 μm with glycol and formalin; later, Jost (1983) tried hydrazine obtaining particles with 0.6 to 5 micron mean diameters. Other reducing agents were ethylene glycol (Ducamp-Sanguesa, 1992; Fievet, 1989) yielding particles of about 0.5 microns, glucose (Zhao, 1996) producing powders of 250 nanometers and hydroquinone (Ryabukha and Kuleshova, 1986), generating silver particles with an average diameter of 1 to 3.5 microns.

It is important to point out that some of the strongest reducing agents, like hydrogen peroxide and hydrazine, produced the largest particles (up to 5 microns). This is possibly related to the faster reduction rates which generate the supersaturation and further precipitation in the solution. This fact would point to the possibility that the control of the reduction rates may bring about a control of the silver powder properties.

Other silver salts that have been used for the production of silver powders by chemical reduction are silver carbonate (Fischer, 1989), silver chloride (Qin, 1988) and silver oxide (Clark and Pickering, 1967). In terms of reducing agents the main one is hydrazine but as mentioned, glucose, ethylene glycol, hydrogen peroxide and hydroquinone have also been studied.

2.2.1 Hydrazine as a Reducing Agent

Hydrazine, N_2H_4, is the simplest diamine. It can essentially reduce all the metals of the transition, lanthanide and actinide series either to a lower valence or to the uncharged state. As a strong reducing agent, hydrazine is used for corrosion control. The hydrazine reduction of silver salts produces monodisperse, small and pure powders. Additionally, the reduction with hydrazine has high production yields (Qin, 1988). This fact together with that one mole of hydrazine reduces four moles of silver makes the production of silver powder by reduction with hydrazine relatively inexpensive.

The solution of hydrazine in water is alkaline. The reaction between water and hydrazine can be expressed by the following equilibrium.

$$N_2H_4 + H_2O \longleftrightarrow N_2H_5^+ + OH^-$$

with a reaction constant of 8.5×10^{-7} at 298 K.

The oxidation mechanism of the hydrazine (Lu and Chen, 1981) can be written as follows:

Overall reaction: $N_2H_4 \longleftrightarrow N_2 + 4H^+ + 4e^-$

$N_2H_4 \longleftrightarrow N_2H_2 + 2H^+ + 2e^-$

$2N_2H_2 \longleftrightarrow N_4H_4$

$2N_2H_2 \longleftrightarrow N_2 + N_2H_4$

$N_2H_2 \longleftrightarrow N_2 + 2H^+ + 2e^-$

As we can see by these reactions, at a low pH, which means a high concentration of H^+ ions, the tendency is that no more electrons will be liberated because of the equilibrium. Because of this, when adding an acid to the reacting solution, the reduction of silver nitrate can potentially be quenched.

2.2.2 Control of Silver Particle Production by Chemical Manipulation

As mentioned, the production of silver particles by precipitation is a very complex process influenced by a variety of rates. The manipulation of any of this rates, as long as it is critical in the process, will bring about a modification in the properties of the resulting silver powders. In the study of production of silver particles by precipitation of its salts, two steps are mostly targeted for the control of particle size distributions. These are the reaction rate and the agglomeration of crystals.

2.2.2.1 Control of Precipitation by Complex Formation

The most simple way to control the precipitation of powders is by controlling the reaction rate. The modification of the concentrations of the reactants, the silver salt or the reducing agent, causes variations in the reduction rate, resulting in the production of powders of different particle size distributions. When the silver salt and reducing agent are selected, and the concentration variation is not enough to control the reaction rate, complexing agents play an important role. By the addition of a complexing agent the decrease of the rate of reaction can normally be achieved.

In the case of silver nitrate reduction by hydrazine, the reaction takes place at a very high rate, even at low hydrazine and silver nitrate concentrations (James, 1909; Freundlich, 1937). Because of this, complexing agents have been a popular alternative for the rate control in this reaction. Ammonia, thiosulfate and ethylenediamine tetraacetic acid have been characterized as strong silver complexing agents that may affect the silver precipitation process (Blokhina et al., 1992; Fléchon et al., 1972; Cheng and Xia, 1993; Fiorucci et al., 2000).

Particularly, ethylenediamine tetraacetic acid (EDTA) is a very interesting compound for the complexing of silver ions. EDTA exists in solution as the ethylenediaminetetraacetate anion with a charge of minus four plus four hydrogen cations, and is referred to by the notation Y^{4-}. Due to the its strong complexing power with several metal ions, EDTA is used both for industrial and analytical purposes (Pribil, 1982).

One mole of EDTA can form complexes with one to four moles of silver (I) (Fiorucci et al., 2000), but under an excess of EDTA the one to one complex (AgY^{3-}) prevails. The complex AgY^{3-} has a formation constant of 1.93 x 10^4 M^{-1}, and the relevant solubility products are $K_{S0} = [Ag^+]^4[Y^{4-}] = 9.0 \times 10^{-18}\ M^5$ and $K_{S1} = [Ag^+]^3[AgY^{3-}] = 1.74 \times 10^{-12}\ M^4$ (Saran et al., 1995). When exposed to an excess of silver cations, the Ag_4Y species is formed as a precipitate. This information must be considered when running silver precipitation experiments under the effect of EDTA.

2.2.2.2 Assistance of Protective Agents in Particle Size Control

Another common method to control the size distribution of particles produced by precipitation, particularly in the case of silver powders, is the use of protective agents. The main mechanism by which these protective agents control the particle size is by the suppression of the agglomeration. However, depending on the protective agent used they can operate on different levels.

The most common protective agent used in the production of ultrafine silver powders is the polyvinyl pyrrolidone (PVP), which has proven to reduce the mean particle diameter from several microns to even 100 nm (Ducamp-Sanguesa et al., 1992; Ayyappan et al., 1996; Chou et al., 1999). Polymer protective mechanisms originated from colloidal chemistry, suggesting this that a complex of the polymers and the metal ions is formed (Hirai et al., 1979). In the case of PVP, after forming the complex with silver, it favors the reduction of complexed silver over free silver ions, as it allows complexed silver to receive more electronic clouds. Hence, nucleation is favored over crystal growth due to steric effects. Also for this reason, particle aggregation is avoided (Zhang et al., 1995).

Other protective agents commonly used for the production of silver ultrafine particles are the polyvinyl alcohols (PVA) (Chou et al., 1999). The general mechanism of particle size control is very similar in all protective agents used, as they are similar polymeric compounds. Even when the cause of the particle size control is a silver complexing mechanism, it is clear that the effect on the rates is very different than the traditional complex one. As the traditional complexes control the powder properties by the manipulation of the reaction rate, the protective agents also complex the silver ions but affect the particle size distribution by an effect on the crystallization kinetics.

CHAPTER 3. Materials and Methods

3.1 Materials

The reactants used in the silver precipitation experiments were all of reagent grade. Silver nitrate and hydrazine hydrate were provided by Altrich CO. USA. Ethylene diamine tetraacetic acid was purchased from Fischer Ltd. Of Montreal, Quebec. For the preparation of all the solutions, distilled water was used. Regarding the control of pH, ammonium hydroxide, nitric acid, and commercial buffers of pH 4, 6, 7, 8 and 10 were used. Also, a 1 M solution of sodium thiosulfate was used in order to quench the reaction.

3.2 Apparatus and Experimental Procedure

The experiments were carried out in a one liter round bottom flask. The temperature was measured in every experiment with a thermometer and in some experiments a constant temperature bath was employed. The reactor was also equipped with a stirrer and a pH meter.

Initially, the silver nitrate solution (various concentrations) was put in the reactor. Afterwards, the complexing agent and buffer, when used, were added to the silver nitrate solution. At a given time, counting time equal to zero, the hydrazine solution was added to the reactor. In the case of batch operation, the addition of hydrazine took less than five seconds. When semibatch operation was used, hydrazine was added with a peristaltic pump at a constant rate.

The reactive mixture was stirred for 5 to 30 minutes, achieving the complete precipitation of silver. During this time, 10 mL samples were taken in intervals of half a minute to two minutes. Samples were filtered immediately after being taken through filters with pores of 0.1 micron diameter. As will be shown in Section 5.1.2, thiosulfate forms a very strong complex with silver. Therefore, after the sample filtration 1 mL of sodium thiosulfate 0.1 M solution was added to avoid further silver reduction. Samples were afterwards analyzed for silver and hydrazine concentrations afterwards.

3.3 Silver and Hydrazine Analysis

The determination of silver concentration was carried out by atomic absorption spectroscopy with an Induced Coupled Plasma analyzer. In this, the sample is introduced into the system and nebulized with argon as a carrier gas. The liquid droplets enter the plasma discharge where the solvent (water) is evaporated, leaving microcrystalline solid particles that contain the silver atoms either in molecular or ionic salt form. The plasma discharge evaporates the solid particles and excites the silver atoms in the gas phase. When the silver atoms return from the excited state to their ground state, the excess energy is carried off through the emission of a photon. Being the difference between excited and ground states characteristic of each element, the energy, and therefore wavelength of the photon released by the relaxation of a silver atom is characteristic of this element. Based on this, and by comparison with the light emitted by standards of known concentration, the silver concentration in the samples can be determined.

The silver concentration determination method presents a problem for the present study. The concentration determined is that of the total silver. This is because the present method does not differentiate free silver ions from complexed silver ions. Moreover, the presence of elemental silver particles of such size that they can be evaporated by the plasma discharge may also be detected by the atomic spectroscopy. Therefore, if particles smaller than the filter pore size (100 nm) are precipitated, the silver concentration determination will be strongly affected.

In terms of the hydrazine concentration, the determination was carried out by the method described by Watt and Chrisp (1962). In this method, hydrazine is mixed with an excess of p-dimethyl-aminobenzaldehyde. These two compounds form a yellow colored complex which follows the Lambert and Beer's laws. Hydrazine being the limiting reactant, the amount of complex formed is proportional to the hydrazine concentration. Consequently, visible spectrometry allows the determination of the hydrazine concentration. The hydrazine concentration determination method presented problems that will be shown in section 4.3.1.

3.4 Scanning Electron Microscopy (SEM)

In order to characterize the produced silver powders, SEM pictures of several samples were taken. The purpose of the SEM pictures is the general examination of the effect of the experimental conditions on the particle size of the silver powders. Single drops of the experimental reaction solutions were taken at given times and placed on a metallic plate. Immediately afterwards, the samples were put in the oven at 100°C in order to dry them. These samples were then directly observed under the microscope.

As multiple species are present in the reactive suspension, the drying of the samples brings about the crystallization of such species and a multiplicity of crystals different in size, morphology and most important composition in the observed samples. For this reason, X-ray diffraction was used to differentiate the pure silver particles from the rest of the crystals.

CHAPTER 4. Preliminary Experiments

As stated in the Introduction, the reaction of reduction of silver nitrate with hydrazine is an extremely fast one. The decrease of the silver concentration as a function of time in the absence of a complexing agent is presented in Figure 4.1. This experiment was carried out at room temperature (20°C).

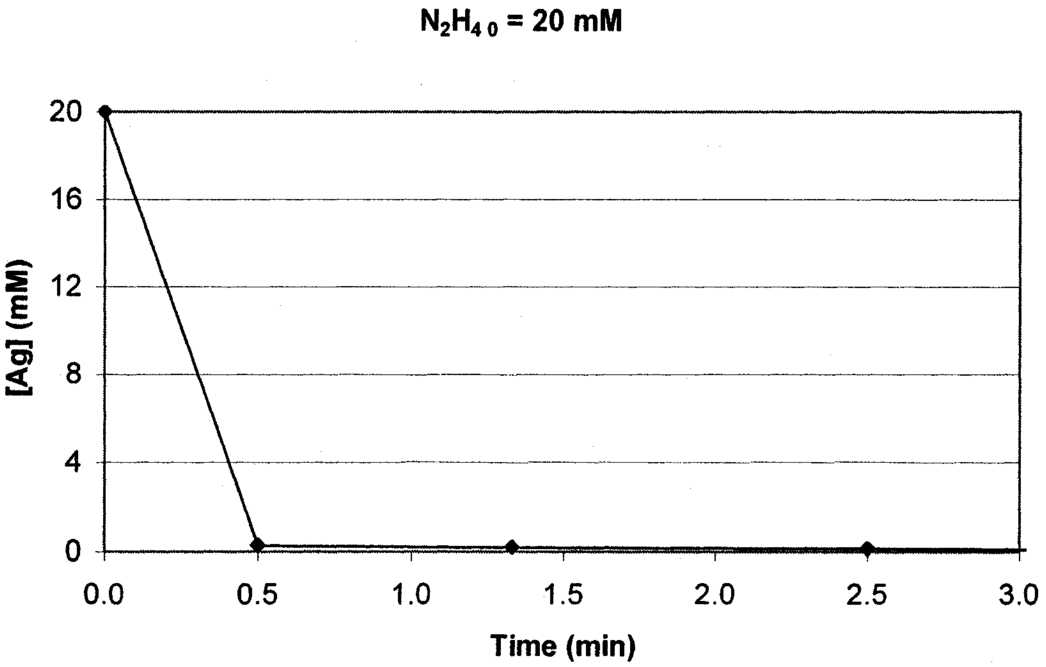

Figure 4.1: Decrease of silver concentration in the absence of a complexing agent

As the graph shows, thirty seconds after the addition of hydrazine, the silver concentration decreased from 20.0 to 0.280 mM. This corresponds to a 98.6% conversion of silver ions.

The fast reaction rate found has several disadvantages. The first one is related to the actual production of silver particles. At such a high rate, the properties of the powders, such as size, morphology and particle size distribution cannot be controlled. Secondly, it is possible for the silver to precipitate on any available surface such as the reactor walls, impellers and feed tubes. In fact, in most experiments carried out under such conditions in the laboratory, the glass walls of the reactor were covered with silver giving it a mirror like finish. Finally, from the experimental point of view, the determination of the kinetics of the reaction demands sequential sampling within very small time intervals.

4.1 Manipulation of the Reaction Rate by Process Variable Modification

4.1.1 Effect of Reactant Concentration and Temperature

The rate of any reaction depends mainly on the concentration of the reactants and the temperature of the reactive mixture. In order to try to control the silver reduction rate by the simple modification of these parameters, several experiments were carried out. The first set was related to the reactant concentrations. Initial silver concentrations of 20, 5, 1 and 0.22 mM were used. Figure 4.2 shows the very fast decrease in the silver concentration for the later three experiments as a function of time at room temperature. This fast decrease is further illustrated when the normalized concentration (normalized to the initial concentrations) is plotted in Figure 4.3.

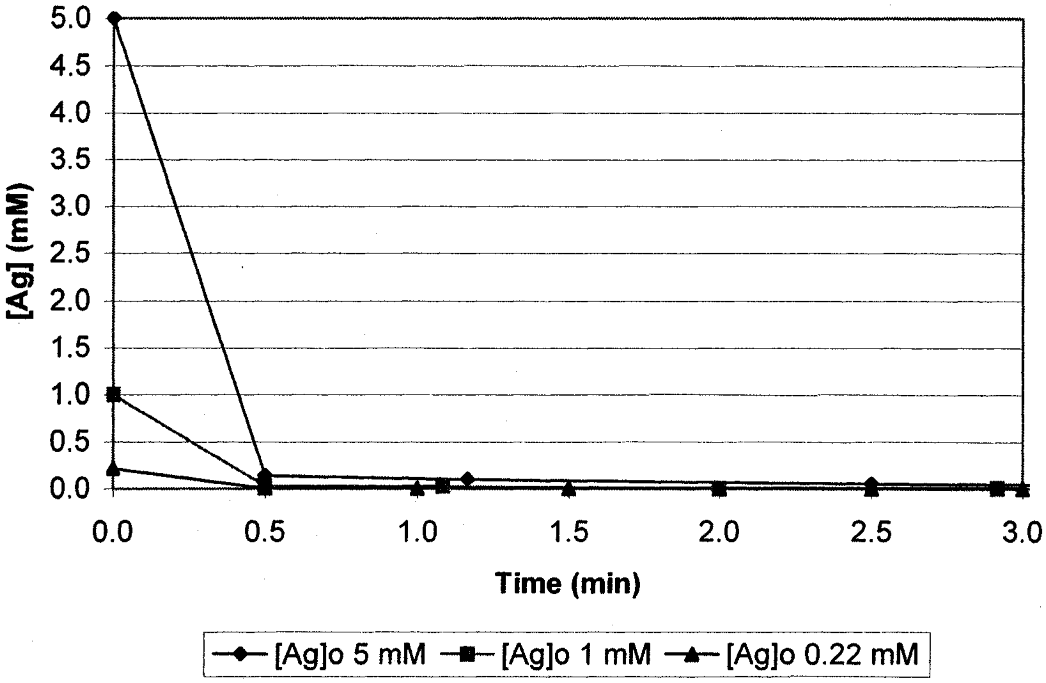

Figure 4.2: Effect of initial concentration on the decrease of silver concentration without a complexing agent

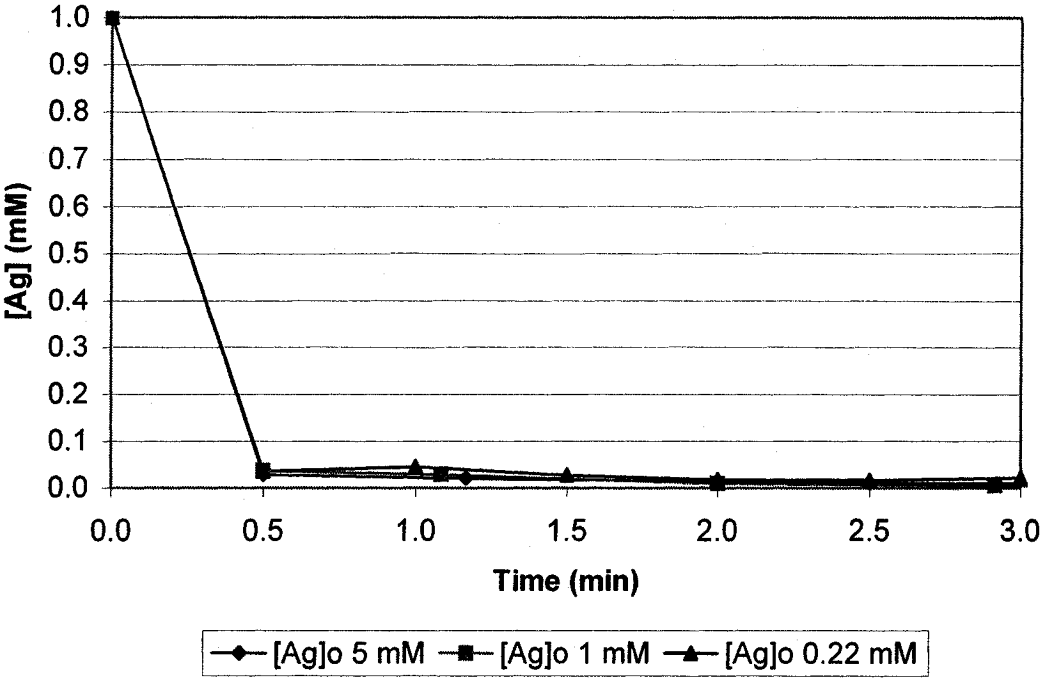

Figure 4.3: Effect of initial concentration on the normalized silver concentration without a complexing agent

This figure shows that even at the lowest concentration of 0.222 mM silver, a 96% conversion is achieved within the first thirty seconds. Moreover, it is possible that the reduction takes place within only a couple of seconds; however, as the first sample was taken at thirty seconds this cannot be determined. Such a large conversion makes clear that even at very low concentrations the reduction of silver with hydrazine is a reaction too fast to be evaluated, at least with this experimental setup. In all these experiments the silver to hydrazine ratio was kept at constant value of 0.74 to 1. A similar experiment with an initial concentrations of 0.225 mM for silver and 0.15 mM for hydrazine gives the same result (data not shown).

The other important parameter that affects the rate of reaction is the temperature. Experiments were carried out at temperatures lower than 21°C. Figure 4.4 shows the concentration of silver as a function of time at a temperature of 0°C.

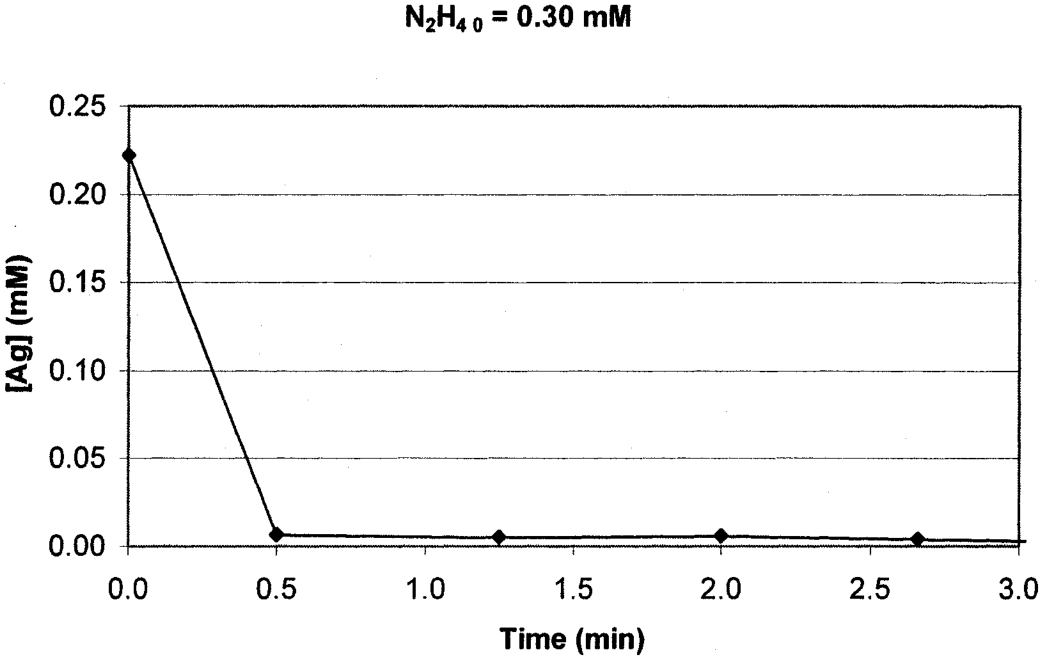

Figure 4.4: Silver concentration as function of time at T = 0°C

Even at this temperature the silver concentration decreases from 0.222 mM to 0.0065 by the time at which the first sample is taken, that is 30 seconds. This corresponds to a consumption of 97% of the initial silver. To summarize, the precipitation of silver by reduction with hydrazine is extremely fast even at very low temperatures and silver and hydrazine concentrations.

4.1.2 Effect of pH on Reduction Rate

As was mentioned in Section 2.3.1, pH has an important effect on the reductive power of hydrazine. Therefore, experiments were carried out at different pH values. It was expected that at low pH values the reduction of silver nitrate would be slowed down or even quenched. Experiments were performed at pH 3, 6, 8 and 10. In these experiments the initial silver concentration was 0.222 mM, and the initial hydrazine concentration was 1.14 mM. The pH was initially set by the addition of either nitric acid or ammonium hydroxide, depending on the acid or basic nature of the experiment. Table 4.1 shows the results obtained from these experiments.

Table 4.1: Effect of pH on conversion after 30 seconds

Initial pH	Final pH	[Ag] (mM)	Conversion (%)
3	3	0.007	96.8
6	5.8	0.008	96.4
8	7.7	0.0065	97.0
10	9.4	0.008	96.4

The results show that the reduction of silver with hydrazine takes place at a very fast rate regardless of the initial pH at which the reactants are placed, with conversions of over 96% in every case and very low initial silver and hydrazine concentrations. The variation of pH during the experiment was very small.

4.2 Reaction Stoichiometry Determination

As stated in the Introduction, depending on the conditions of the reaction mixture, hydrazine can act as a reducing agent by releasing either two or four electrons according to the following reactions;

$$N_2H_4 \longleftrightarrow N_2 + 4H^+ + 4e^- \tag{4.1}$$

$$N_2H_4 \longleftrightarrow N_2H_2 + 2H^+ + 2e^- \tag{4.2}$$

Depending on which reaction takes place, it can be transformed into either elemental nitrogen (N_2) (equation 4.1) or an intermediate compound (N_2H_2) (equation 4.2). For this reason, two or four moles of silver can be reduced with one mole of hydrazine, giving two possibilities for the main reaction stoichiometry.

All the results previously shown were obtained from experiments carried out in a batch reactor and with excess hydrazine. Typical hydrazine to silver ratios were from 5:1 to 1:1, while stoichiometric ratios are 0.5:1 or 0.25:1 depending on the level of oxidation of hydrazine. In order to establish which of the two reactions takes place, experiments were carried with excess silver. Figure 4.5 shows data obtained with a silver to hydrazine ratio of 4:1, with initial silver concentration of 0.27 mM. The pH at which the experiment was carried out was 4.

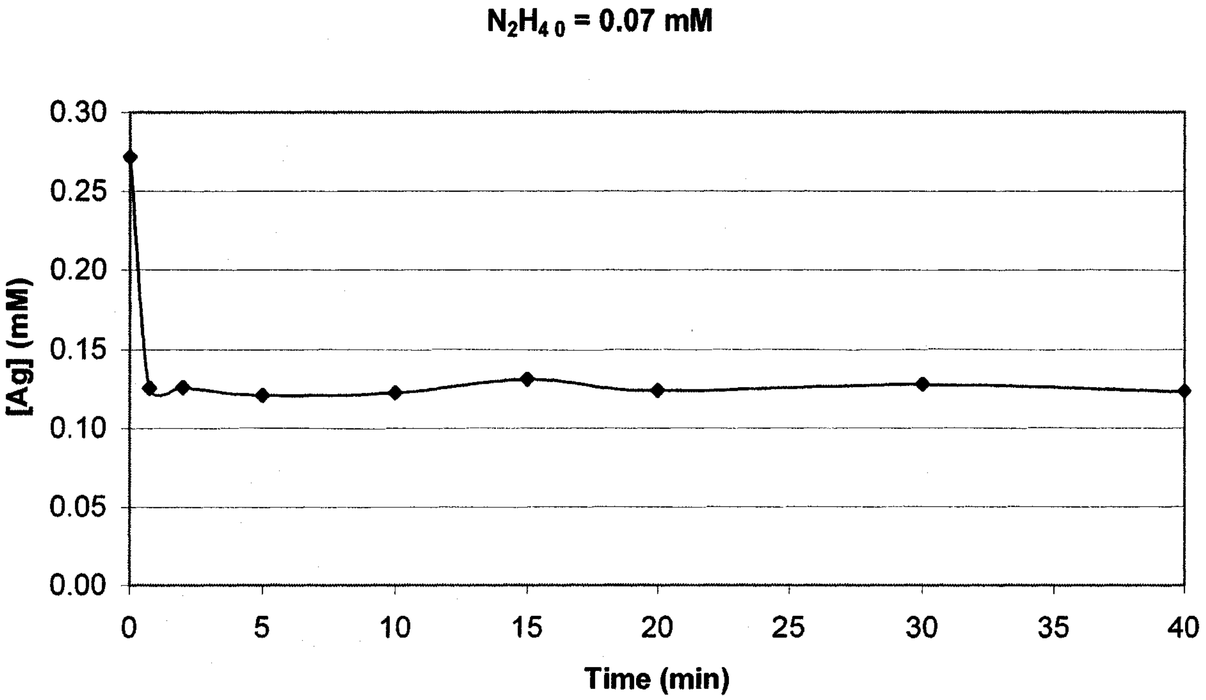

Figure 4.5: Silver concentration with hydrazine as limiting reactant

As with the previous experiments, most of the decrease in the silver concentration took place within the first half minute, when the first sample was taken and after which the silver concentration remains practically constant at 0.125 mM. By difference with the initial value we know that 0.145 milimoles of silver per liter have been reduced. Assuming that all the hydrazine that was initially present has completely reacted (0.07 mM), the ratio of silver to hydrazine reacted can be calculated, thus obtaining the stoichiometry of the reaction. In this case, the reacted silver to hydrazine ratio is 2.08 to one. This implies that the reaction taking place is the one expressed in equation 4.3.

$$2\ Ag^+ + N_2H_4 \longleftrightarrow 2\ Ag^\circ + N_2H_2 + 2\ H^+ \qquad (4.3)$$

The assumption that all hydrazine reacted was tested by measuring the hydrazine concentration with a spectrophotometric method. Problems regarding this determination will be discussed later in this chapter.

In order to confirm this stoichiometry, a semi batch experiment was carried out. In this experiment the silver solution was placed in the reactor and the hydrazine was added at a rate of 6.4 x 10^{-3} milimoles per minute. Samples were taken, filtered and analyzed for silver content. Figure 4.6 shows the results of this analysis. Also, this Figure shows the total amount of hydrazine added to the reactor at any given time.

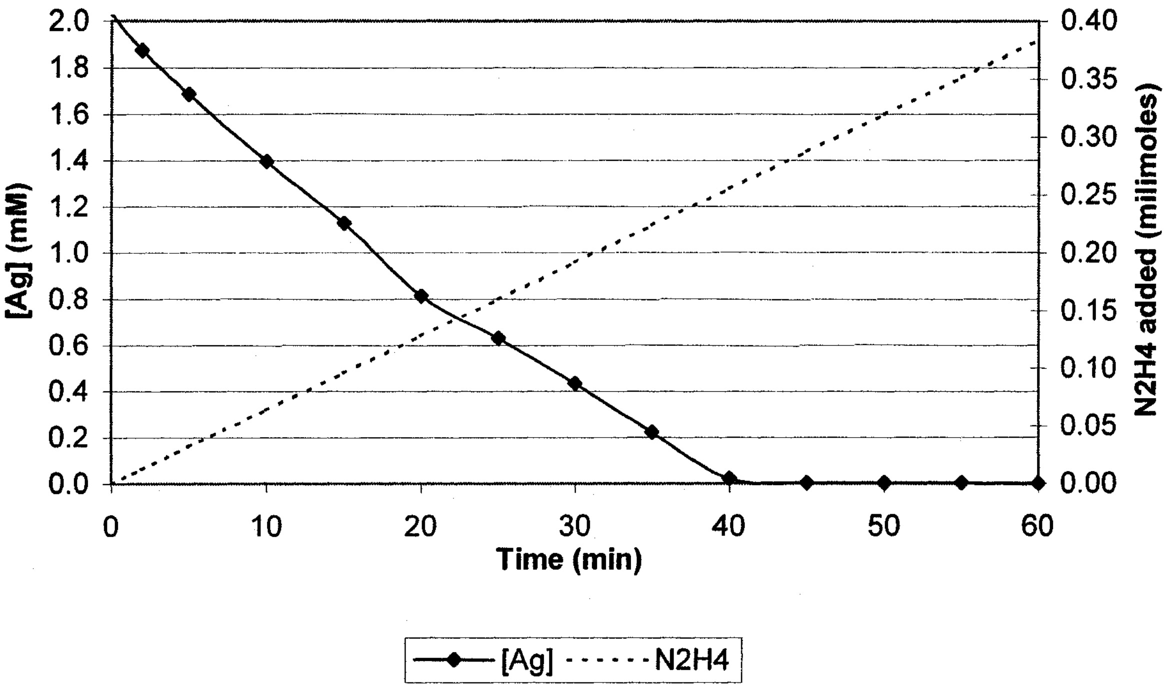

Figure 4.6: Variation of the silver concentration and total amount of hydrazine added in semibatch reactor, pH 4, initial volume 300 ml with molar flow of hydrazine 6.4x10^{-3} milimoles per minute

In order to have a clear understanding of the reaction stoichiometry, another set of data of silver reduced against hydrazine oxidized is needed. Having such a fast reaction, it is necessary to carry out the reaction by operating the reactor under a semibatch mode in order to get more than one silver to hydrazine reaction proportion.

To achieve this, the amount of reduced silver was calculated at every sampling time for the results shown in Figure 4.6. The values obtained were plotted against the milimoles of hydrazine added until the time each sample was taken. Since the reaction is assumed to take place instantaneously, the amount of hydrazine added corresponds to that of hydrazine reacted. Figure 4.7 shows the amount of silver reduced to the total amount of hydrazine added.

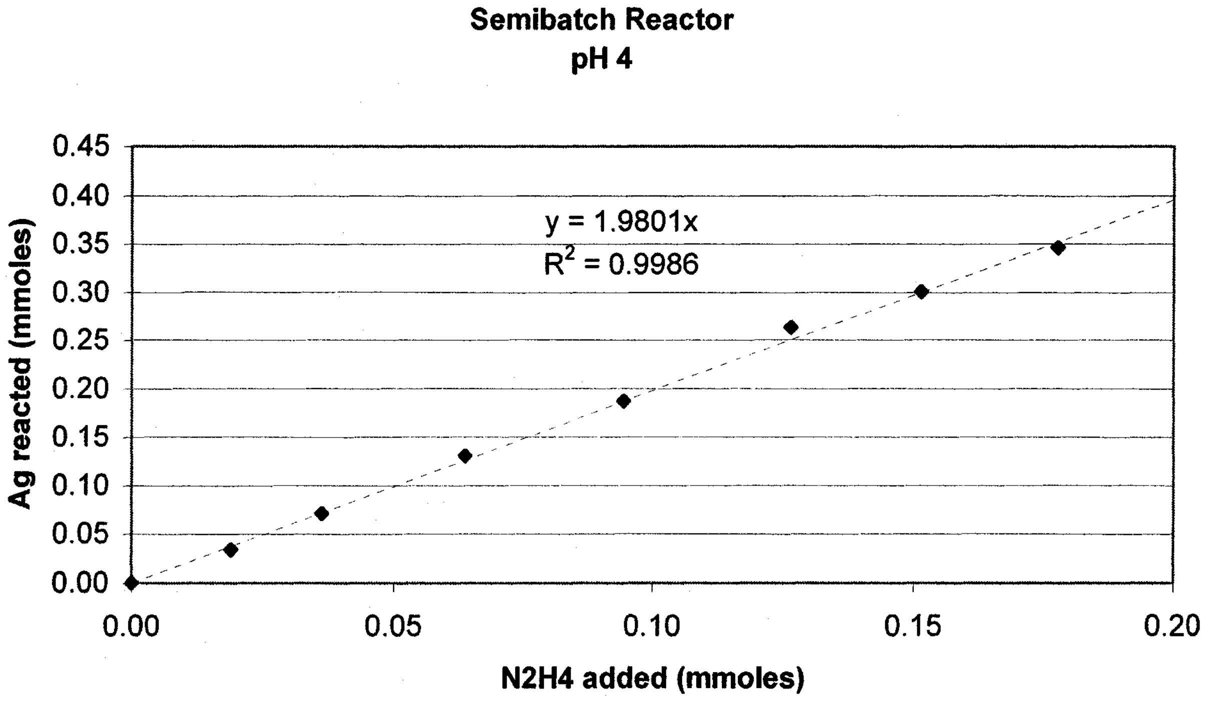

Figure 4.7: Milimoles of hydrazine added vs milimoles of reduced silver in semibatch reactor, pH 4

The experimental data present a clear linear pattern with an ordinate of zero and slope of 1.98 confirming the previous result. This experiment was also performed at a pH of 4.

Similar semibatch experiments were carried out at the higher pH values of 6, 8 and 10. Figure 4.8 shows the concentration of silver and amount of hydrazine added for the experiment carried out at pH 10.

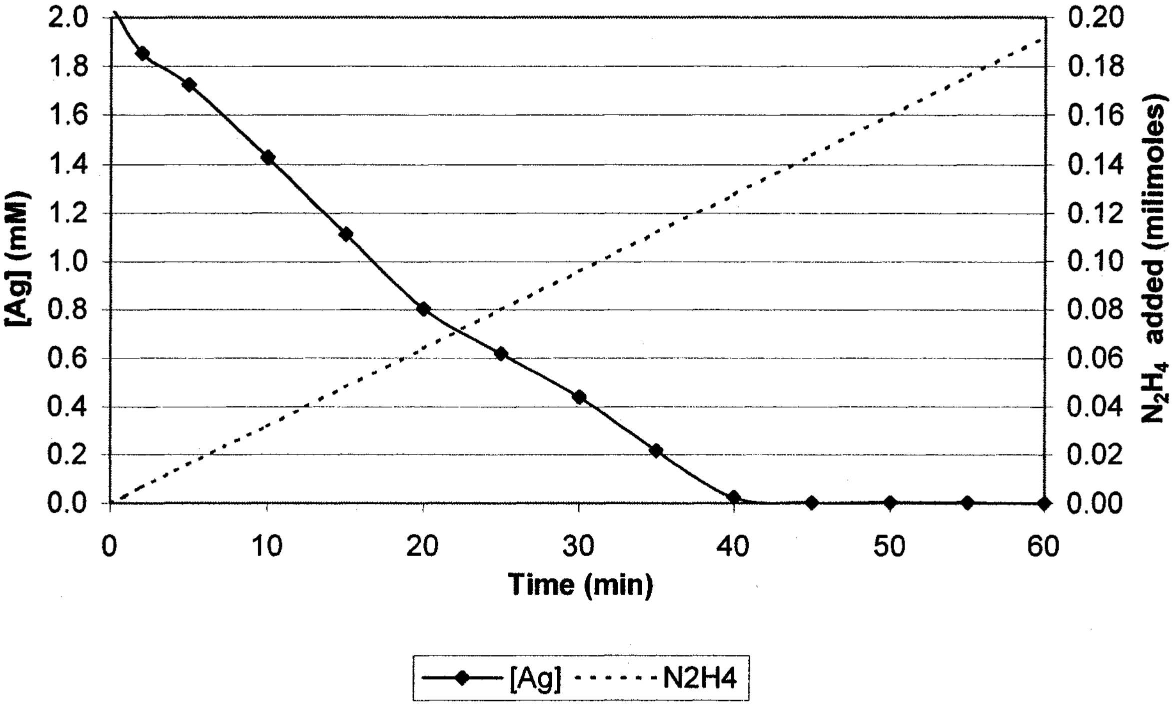

Figure 4.8: Variation of the silver concentration and total amount of hydrazine added in semibatch reactor, pH 10, initial volume 300 ml with molar flow of hydrazine 3.2×10^{-3} milimoles per minute

From this data the quantity of silver reacted was calculated and plotted against the total hydrazine added. Figure 4.9 shows this results the amount of silver reacted plotted against the total hydrazine added for the experiment carried out at pH 10.

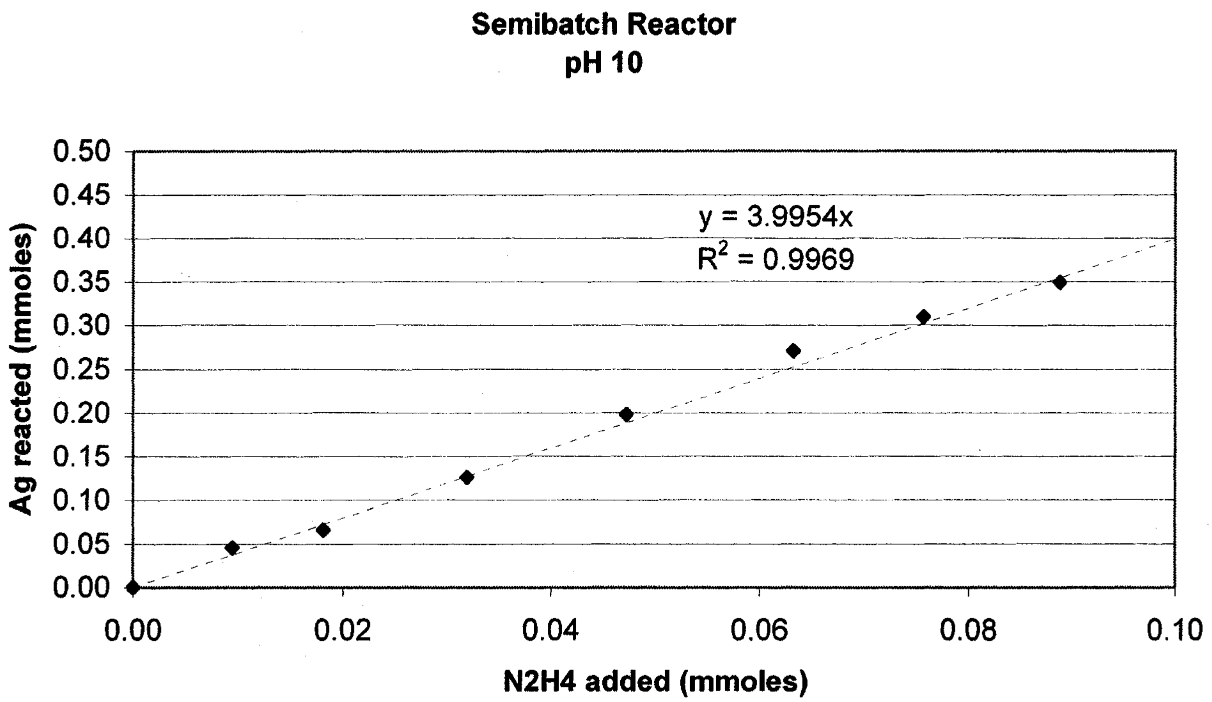

Figure 4.9: Milimoles of hydrazine added vs milimoles of reacted silver in semibatch reactor, pH 10

The slope in this case is 4.0 mmol Ag per mmol hydrazine, having a significant correlation factor. Therefore, the reaction taking place at this pH is the one represented in equation 4.4.

$$4\,Ag^{+} + N_2H_4 \longleftrightarrow 4\,Ag^{\circ} + N_2 + 4\,H^{+} \qquad (4.4)$$

The same stoichiometry was obtained for the experiment carried out at pH 8, while the stoichiometry of equation 4.3 was observed in the experiment at pH 6.

4.3 Problems with the Analysis of Hydrazine and Silver

4.3.1 Hydrazine

A standard analytical technique was applied for the quantification of hydrazine concentrations during the experiments. However, all the previous results were shown in terms of silver concentrations or calculated from these values. No experimental hydrazine values were shown because the hydrazine determination presented some problems. Figure 4.10 presents the values obtained from the analysis for silver and hydrazine concentrations as functions of time for a batch operation with hydrazine as the limiting reactant.

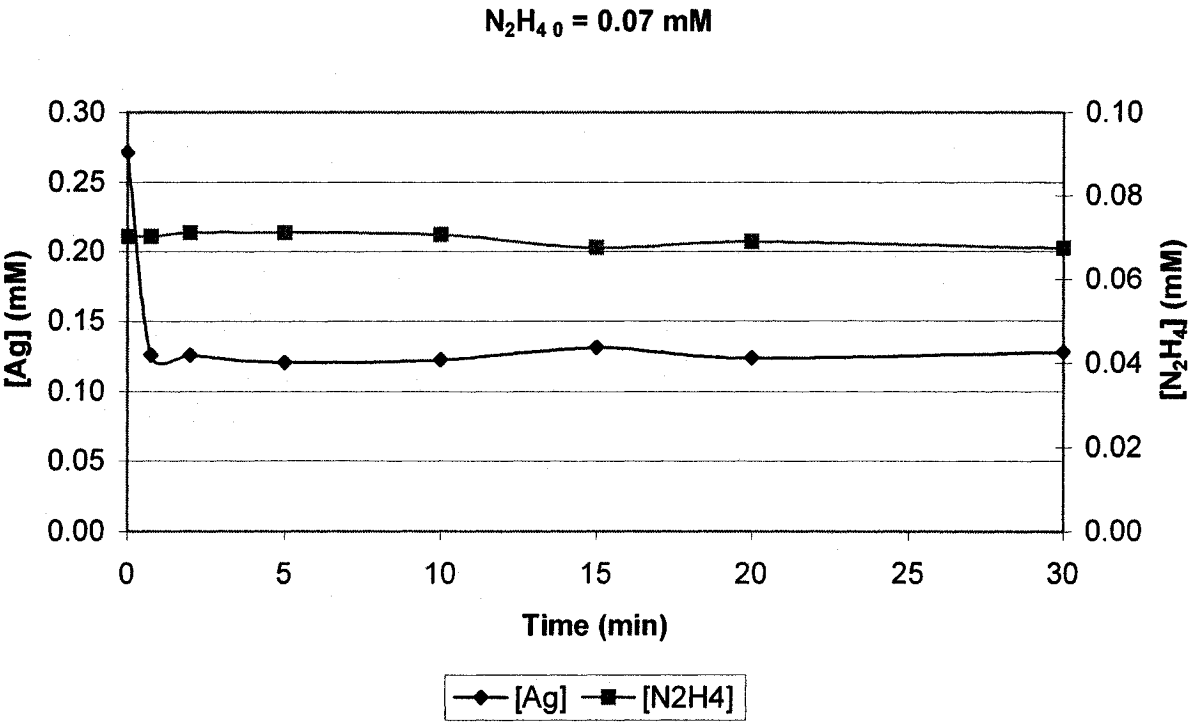

Figure 4.10: Experimental silver and hydrazine concentrations with hydrazine as limiting reactant

This graph shows that the decrease in silver concentration takes place once again before the first 30 seconds. This concentration decreases from 0.27 millimolar to 0.125 milimolar. As this reaction was carried out in an acid medium, the expected hydrazine to silver reaction ratio is 2:1. With this ratio, it would be expected that the hydrazine would go from its initial value of 0.07 milimolar, to almost zero. However, we can clearly see that the hydrazine concentration remains constant all along the experiment. This way, the analytical results would indicate that while the silver ions are being reduced, hydrazine is not reacting. Still, a linear relationship was found between the reacted silver and the total added hydrazine.

The hydrazine analysis was also done for semibatch experiments. In Figure 4.11 experimental silver and hydrazine concentrations are plotted against time. Also, the theoretical hydrazine concentration, assuming no reaction, and the theoretical silver concentration, assuming a total reaction advance, are shown as functions of time.

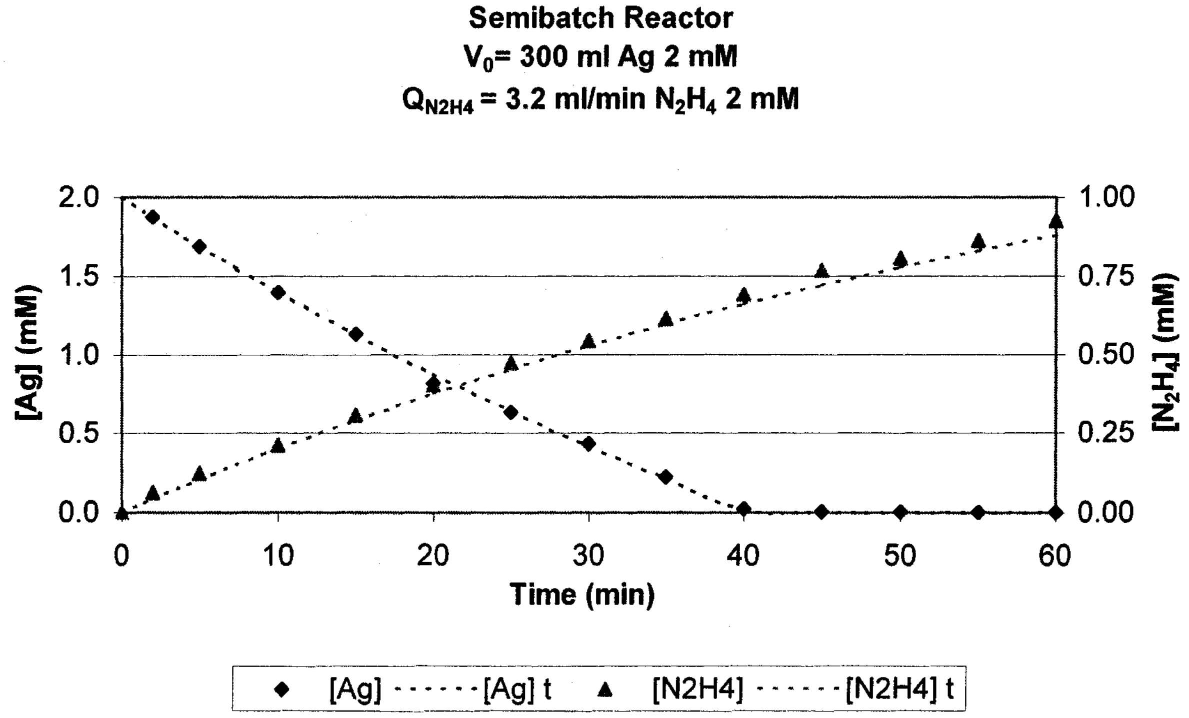

Figure 4.11: Silver and hydrazine experimental and theoretical concentrations in semibatch reactor, pH 4

The theoretical silver concentration was plotted assuming that all the hydrazine added to the reactor was oxidized immediately, reducing two moles of silver ions per mole of hydrazine. The theoretical hydrazine concentration, on the other hand, was calculated by assuming that no reaction was taking place. Clearly, the points of the experimental determination of silver and the function for the theoretical values agree, and indicate that the reaction is taking place in its totality. In contrast, the hydrazine theoretical and experimental curves also match, and therefore suggest that the silver hydrazine reaction is not taking place. This incongruity indicates that there is a problem with either of the analytical techniques.

We know that the silver reduction with hydrazine is a fast reaction. Also, we have found clear relations between the experimental silver values and the total added hydrazine, which are coherent with the probable reactions of oxidation of hydrazine. For these reasons, it is safe to assume that the experimental determination that is generating the problem is the determination of hydrazine. In case these grounds were not enough, we can visually notice that a reaction is taking place, producing insoluble and presumably solid products.

In the case of the hydrazine analysis, it is done by the reaction of hydrazine with p-dimethyl aminobenzaldehyde, which produces a yellow complex. The concentration of this complex is measured using an UV-visible spectrophotometer. We know that the oxidation of hydrazine under a low pH will produce a secondary compound, N_2H_2. Due to the similarity of this compound with hydrazine, there might be the possibility of it reacting to form the colored complex, and therefore, be quantified as hydrazine. Also, the reaction of hydrazine with p-dimethyl aminobenzaldehyde takes place at a very low pH. At this pH, it might be possible that hydrazine is regenerated back from the unstable secondary complex N_2H_2.

The measurement of hydrazine was intended to be done also by simple titration. However, the concentrations of hydrazine found are so low that it was not viable to get precise measurements. Because of the problems in the determination of hydrazine concentrations, all the results from this point on are presented just in terms of silver concentrations.

4.3.2 Silver

As mentioned in Chapter 3, the Induced Coupled Plasma can potentially detect solid elemental silver particles and account these into the silver analysis. In order to prevent this, the samples are passed through a 0.1 micron pore size filter prior to the silver content evaluation. However, particles smaller than the pore size may affect the determination of silver content. Experiments were carried out in order to test the effect of solid silver particles on the silver concentration analysis.

If silver particles smaller than the filter pore size affect the determination of soluble silver, the use of filters with different pore sizes will give different results for experiments ran under the same conditions. The general behavior expected is that for larger pore sizes the decay in the silver concentration will appear later, and will present a slower rate. Experiments were run with four different pore size filters, of 0.1, 0.2, 0.45 and 0.8 microns, and with initial silver, hydrazine and EDTA concentrations of 0.22 mM, 1.1 mM and 1.1 mM respectively, presenting the results shown in Figure 4.12.

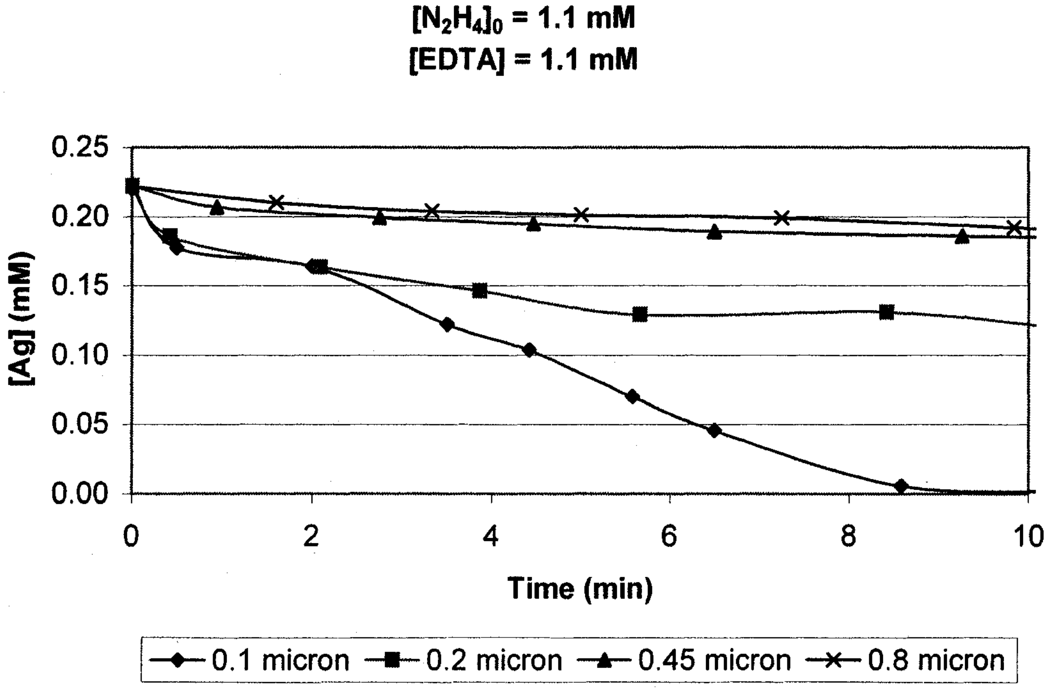

Figure 4.12: Effect of filter size on the observed rate of the reaction

As can be seen in the figure, the use of a filter with different pore size alters the observed silver concentration profile. As predicted, for smaller pore sizes the decrease in the apparent silver concentration takes place earlier. This shows that the analysis of silver by Induced Coupled Plasma accounts for both silver in solution and solid silver particles. Further proof of this will be shown in section 5.4.2.

As the effect of solid elemental silver nanoparticles on the analysis of soluble silver was observed after several experiments had been carried out, some results to be presented later are reported in terms of the apparent silver concentration.

CHAPTER 5. Rate Control with EDTA

As was stated in the previous chapter, the silver reduction with hydrazine proceeds to completion within a very short time due to its fast rate. In order to slow down the reaction and thus control the final particle properties, complexing agents can be used.

5.1 Selection of Chelating Agent for the Silver – Hydrazine Reaction

A series of potentially effective complexing agents mentioned in the literature were tried. Ammonia, thiosulfate, sulfite and ethylendiamine tetraacetic acid (EDTA) were the chelating agents tried to slow down the reaction. However, even if these agents generate a decrease in the particle size of the produced powders, they may not be adequate for the experiments.

5.1.1 Ammonia and Sulfite

The first complexing agents tested was ammonia. Silver forms a complex with ammonia according to

$$Ag^{+} + 2\ NH_3 \longleftrightarrow [Ag\ (NH_3)_2]^{+} \qquad 5.1$$

Experiments were carried out under several ammonia concentrations (1.1, 5.5 and 11 mM) and pH values (4, 7 and 10). In all the experiments, the silver and hydrazine concentrations used were respectively 0.22 mM and 1.1 mM. This concentrations were chosen in order to compare with experiments with no complexing agent reported in the previous chapter. Figure 5.1 shows typical results obtained from one of this experiments.

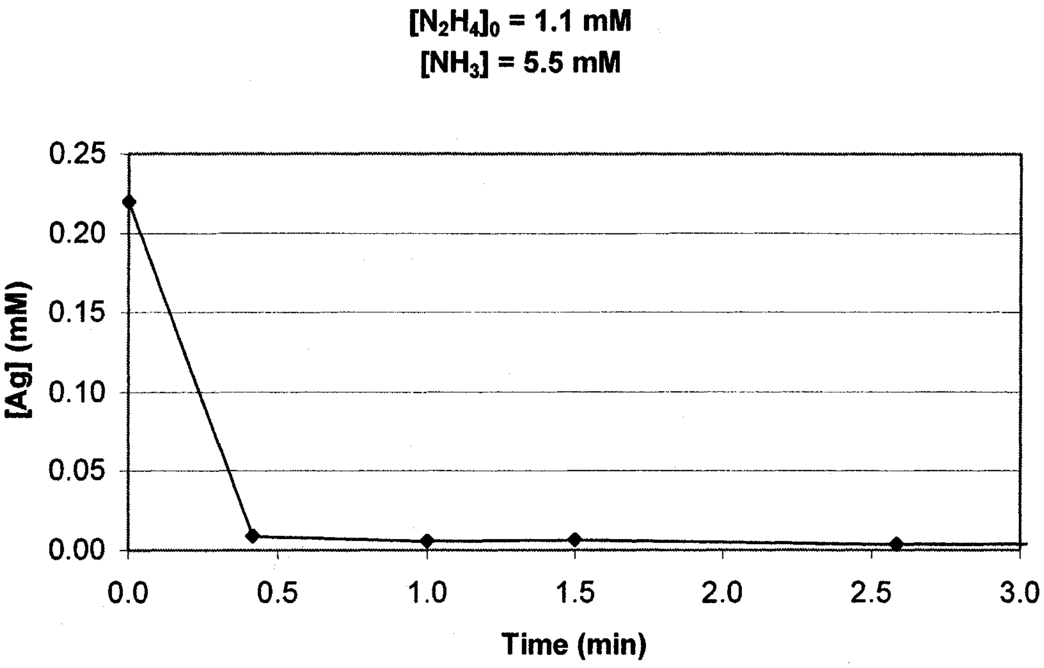

Figure 5.1: Effect of ammonia as complexing agent in silver reduction reaction, pH 7

The first observation for all the pH values and ammonia concentrations was that the silver concentration decreased in over 95% during the first half minute or less. It should be noted that in the experiments the concentration of ammonia used was from 2.5 to 25 times the stoichiometric amount with respect to the initial silver concentration.

Similar results were obtained when sulfite was tested as a complexing agent. The initial silver concentration was again 0.22 while the sulfite concentrations used were from 1.1 mM to 5.5 mM, which represent from 5 to 25 times the stoichimetric amount.

These results indicate that neither ammonia nor sulfite are adequate complexing agents as there is no observable decrease in the rate of the reaction.

5.1.2 Thiosulfate

Thiosulfate forms a strong complex with silver of the form:

$$Ag^+ + 2\ S_2O_3^{2-} \longleftrightarrow [Ag\ (S_2O_3)_2]^{2-} \tag{5.2}$$

Experiments were carried out at the thiosulfate concentrations of 1.1 mM, 0.55 mM and 0.44 mM, and pH values of 4 and 10. The initial silver concentration used was of 0.22 mM, having then thiosulfate in an excess of 2.5 and 1.5 times, and in stoichiometric amount for the last experiment. Figure 5.2 shows typical results obtained in the experiment with lowest thiosulfate concentration, at stoichiometric amount.

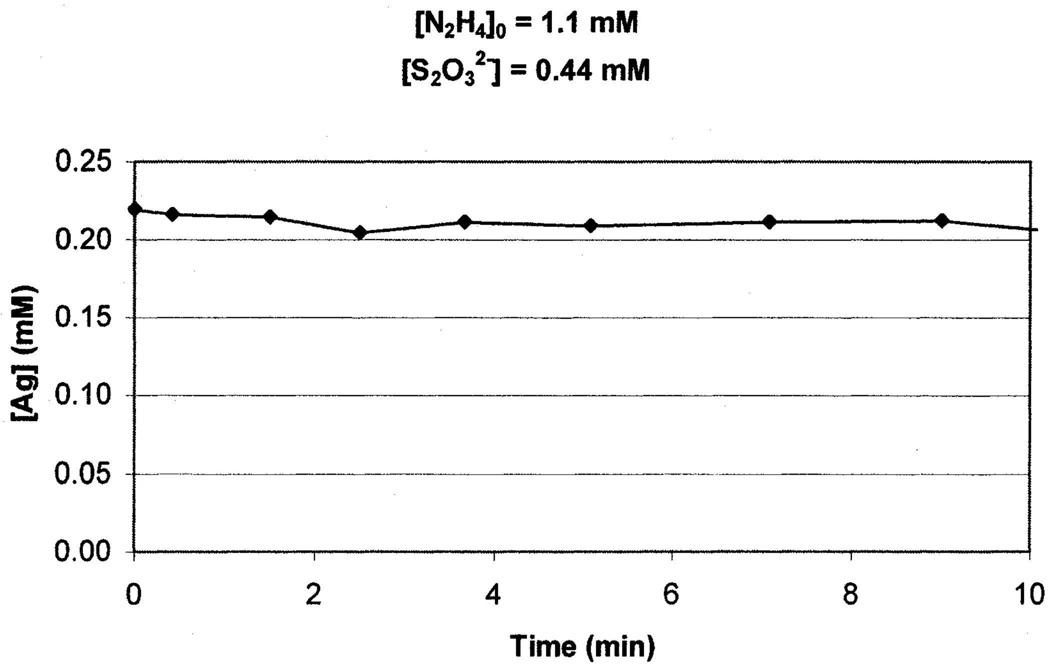

Figure 5.2: Effect of thiosulfate on the silver reduction with hydrazine

Under these conditions, as in every experiment carried out with thiosulfate as complexing agent, the silver concentration remained constant throughout the whole experiment. These results support that the complex formed by silver and thiosulfate, $[Ag(S_2O_3)_2]^{3-}$, is an extremely strong one, not allowing the reduction of silver to take place even at long times. While it is possible that there may be some silver particles that escape the filter, it is not likely because after certain time an agglomeration of particles would take place and a decrease in silver concentration would have been observed.

The experiments with ammonia and thiosulfate show that the reduction of silver strongly depends on the strength of the complex formed. In fact it is known that while the silver – ammonia complex is more of a weak complex, the silver – thiosulfate complex is one of the strongest complexes of silver. This confirms the experimental results described above.

5.1.3 Ethylenediamine tetraacetic acid

As was mentioned in the introduction, ethylenediamine tetraacetic acid (EDTA) forms stable complexes with silver. Preliminary experiments similar to those performed with ammonia, thiosulfate and sulfite were carried out, using this time EDTA, were also performed. Figure 5.3 shows one of the silver concentration profiles obtained for the experiments of EDTA as a complexing agent at pH 7.

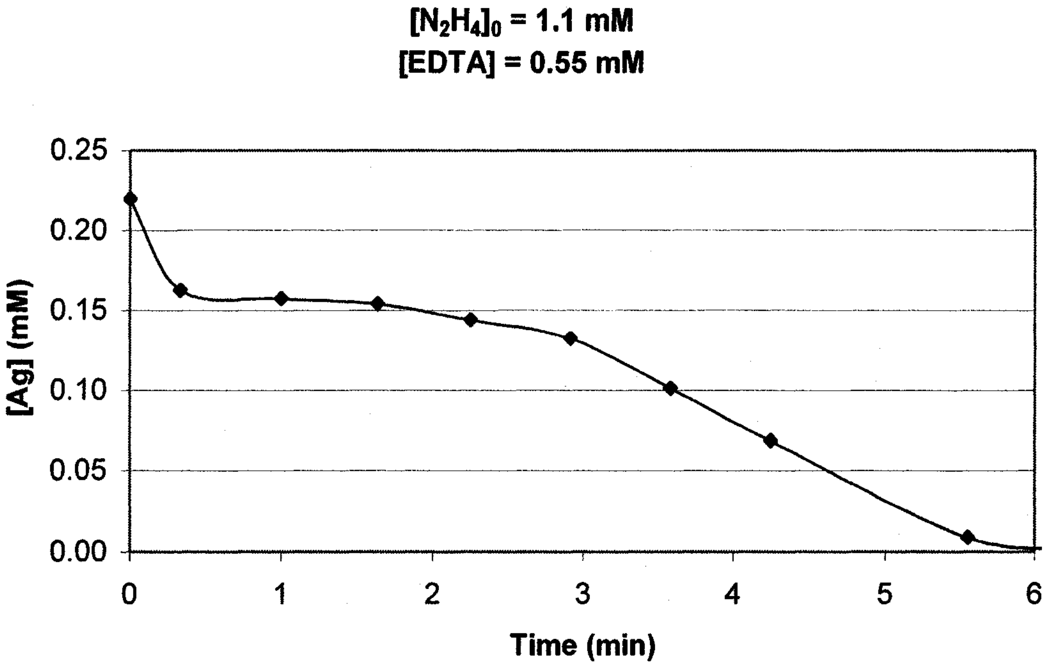

Figure 5.3: Silver reduction with EDTA as a complexing agent

This figure shows that for the experimental conditions the reduction of silver with hydrazine is slowed down under the presence of EDTA, in contrast to ammonia and sulfite. Also, the silver – EDTA complex is not as strong as the silver – thiosulfate complex so as to prevent the reaction from taking place. Because of this, ethylenediamine tetraacetic acid was chosen as the complexing agent to be used in this project.

5.2 EDTA in the Silver Reduction with Hydrazine

5.2.1 EDTA – Ag Complex Formation Time

In order to carry out the experiments it is necessary that the addition of hydrazine takes place after the EDTA – Ag equilibrium has been reached. As there is no bibliographic reference to the EDTA – Ag complex formation and dissociation rates, it is necessary to evaluate experimentally the time it takes for such equilibrium to be achieved. Otherwise, an extra variable, being the time of addition of hydrazine, has to be considered.

Three experiments were carried in order to ensure the correct time of addition of hydrazine. In these experiments the variable treated was the time between the additions of EDTA and hydrazine. This period is referred to as complexation time. The results are shown in figure 5.4.

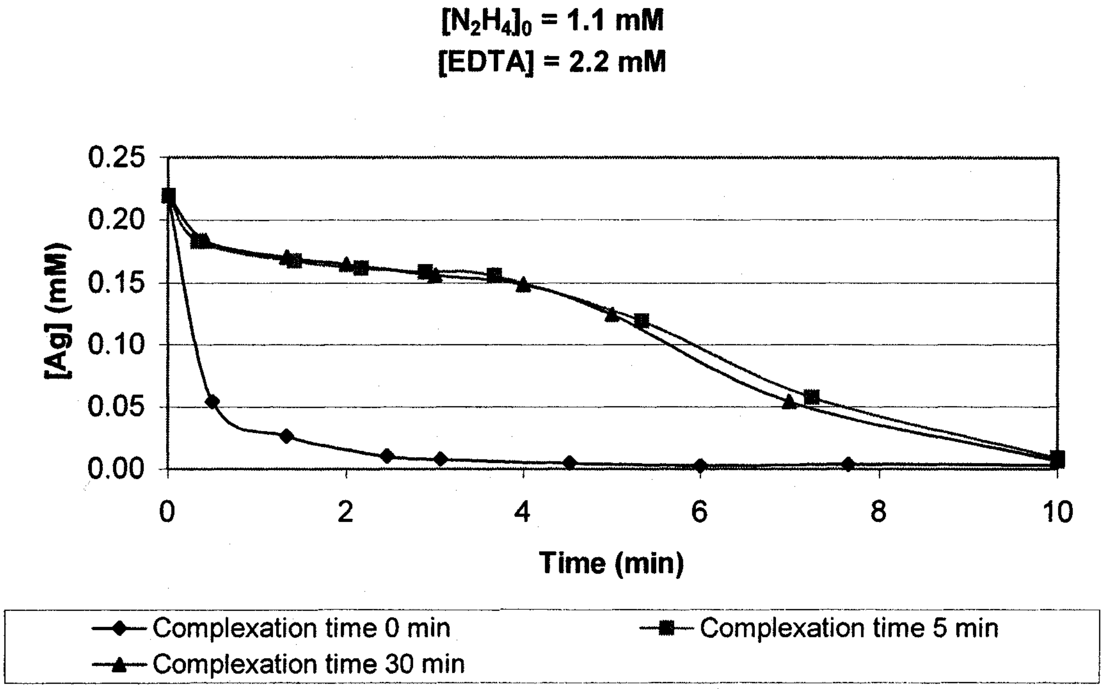

Figure 5.4: Effect of complexation time on silver reduction rate

Three curves are shown in this plot, each corresponding to a different complexation time. When the complexation time is zero, the silver concentration decreases abruptly, similarly to the case where no complexing agent is present. These fast decline implies that the silver reduction rate is larger than the silver – EDTA complex formation rate, at least at the given concentrations.

On the other hand, the experiments with complexation times of 5 and 30 minutes presented just about the same silver concentration profile. This results imply that at a complexation time of five minutes the EDTA – silver mixture has reached an almost stable state, and therefore such complexation time is adequate for the experiments. Since the reactant concentrations throughout this thesis are similar to the ones used in this experiments, a five minute complexation time was used for all the experiments.

5.2.2 EDTA – Ag stability as function of pH

Having selected EDTA as the complexing agent, the conditions at which the reaction will be carried out have to be determined. The first parameter to be studied was the pH because depending on its value hydrazine can reduce silver according to two different stoichiometries. A set of experiments was carried out, keeping the initial silver, hydrazine and EDTA concentrations constant, with values of 0.22 mM, 1.1 mM and 2.2 mM respectively. These experiments were carried out at the pH values of 4, 7 and 10. Figure 5.5 shows the results obtained.

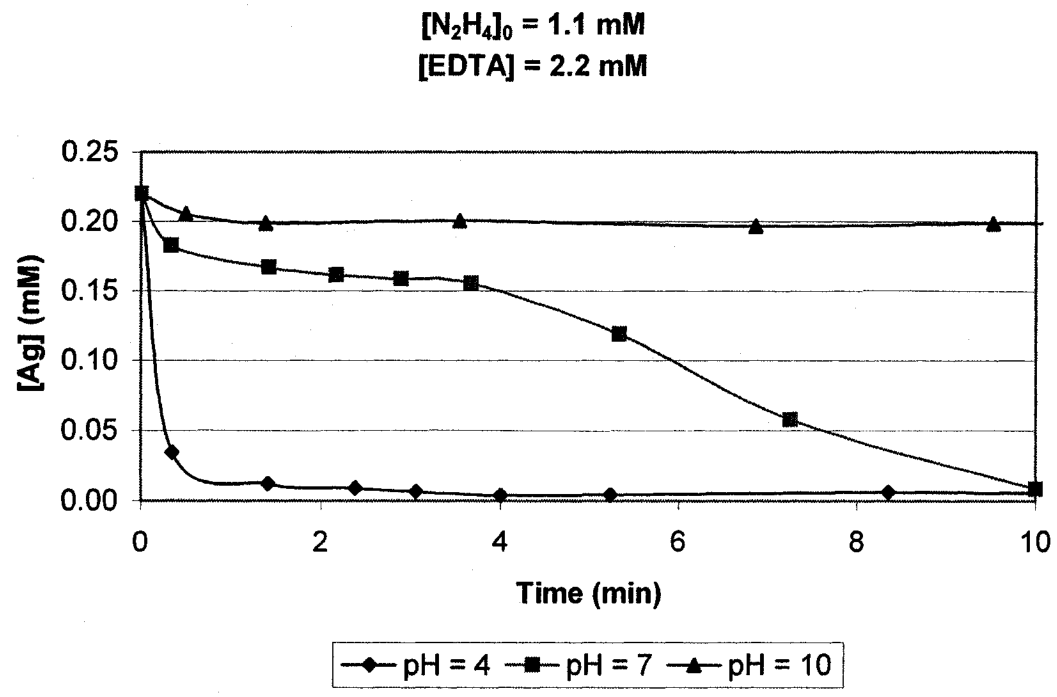

Figure 5.5: Effect of pH on silver concentration decrease in presence of EDTA

As seen, at the most acidic pH tested (pH 4) the initial silver concentration drops from 0.22 milimolar to 15% of its initial value during the first twenty one seconds. Although there is a slight difference with respect to the experiments with no complexing agent, shown in chapter 4, the reaction takes place at a very fast rate.

In contrast, at pH 10 there is a small initial decrease in the silver concentration but after this the concentration remains constant. The total conversion, even after twenty minutes, is only 9.1%.

Finally at the pH 7 experiment, there is a gradual decrease in the silver concentration. Therefore, the experiments presented henceforth were carried out at pH 7 since it appears that the reaction rate can be better controlled. As was shown in section 4.2, hydrazine can present two distinct oxidation levels, releasing either two or four electrons, depending on the pH at which the reaction is carried. By carrying out experiments similar to those in section 4.2 it was found that at pH 7, four moles of silver are reduced with one mole of hydrazine (Eq. 4.4).

5.2.3 Effect of EDTA Concentration on the Reaction Rate

Experiments were carried out at different EDTA concentrations in order to test the effect of the complexing agent on the rate of the silver reduction. Initial silver and hydrazine concentrations were kept constant for the set of experiments, being these 0.22 mM and 1.1 mM respectively. In addition to a blank experiment in the absence of EDTA experiments with EDTA concentrations between 0.22 mM and 3.3 mM were carried out. These concentrations are equivalent to a variation of EDTA from the stoichimetric amount (1:1) with respect to silver to a 15 times excess.

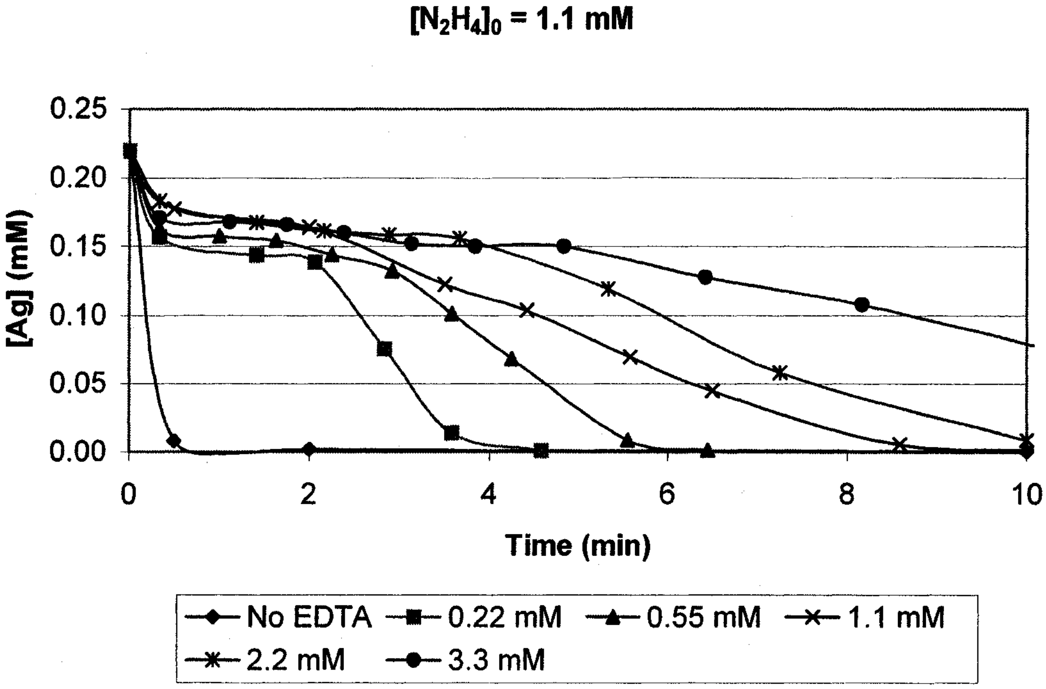

Figure 5.6: Effect of EDTA concentration on the silver reduction rate

The first thing to note is the immediate decrease in the rate of silver reduction under the presence of EDTA at all concentrations. By increasing the EDTA concentration, slower reaction rates are achieved. Also, at each EDTA concentration, the decrease in the silver concentration shows a characteristic pattern. This pattern consists of three stages, as shown in Figure 5.7.

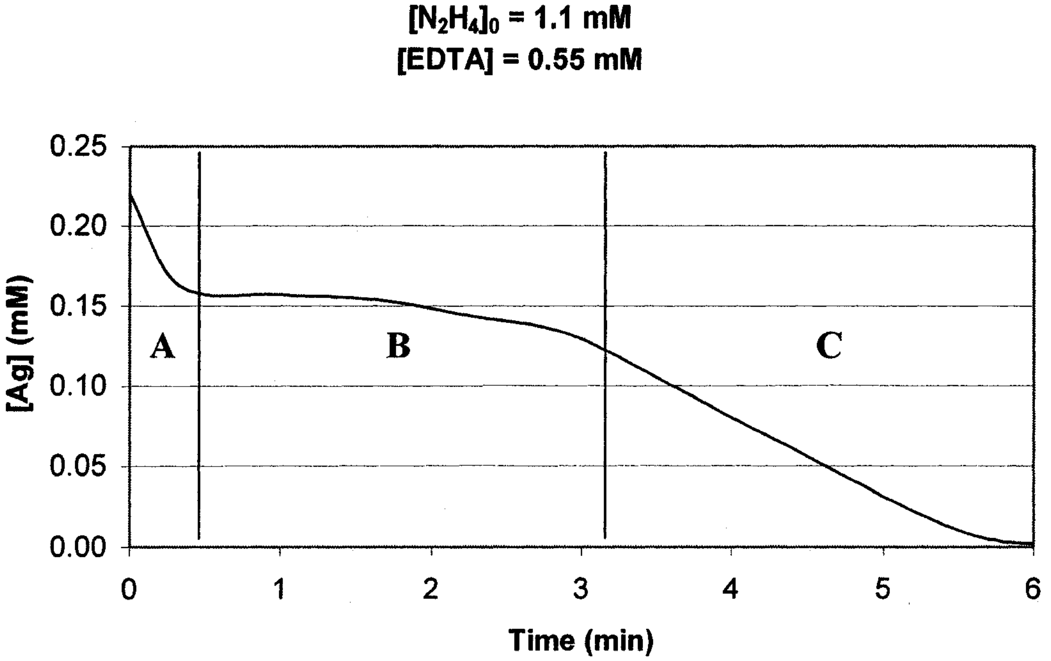

Figure 5.7: Typical behavior observed in silver reduction under the effect of EDTA

In the first stage, marked A in Figure 5.7, there is a fast initial decrease in the silver concentration. This decrease takes place during the first half minute of the experiment, or probably even less. After this and until the third minute, there is a second stage (B) in which the silver reduction rate drops down to almost zero and therefore the silver concentration stays practically constant. Finally, there is a third stage (C) in which a gradual decrease in silver concentration can be observed, until the silver content drops to zero. This pattern will be encountered in all subsequent experiments and an attempt will be made to explain it.

Such a pattern is not the expected one because of the following reasons. We know that the total EDTA concentration, i.e. free plus complexed EDTA, stays constant. Also, the concentration of hydrazine decreases along with the silver concentration; since it was added in excess, only about 10% of the hydrazine will have reacted when all silver is reduced. Thus, for given hydrazine and EDTA initial concentrations, as well as constant temperature and pH, the rate of the reaction is expected to be exclusively a function of the silver concentration, having a lower rate for smaller silver concentrations. Nevertheless, we can see from Figure 5.7 that the rate of the reaction does not decrease with the silver concentration throughout the experiment.

5.2.4 Effect of hydrazine and silver concentration on the reduction rate

Experiments were also carried out at hydrazine concentrations of 0.45, 0.9, 1.35 and 1.8 mM. The EDTA and silver concentration were respectively 1.1 mM and 0.22 mM. Figure 5.8 shows the results obtained.

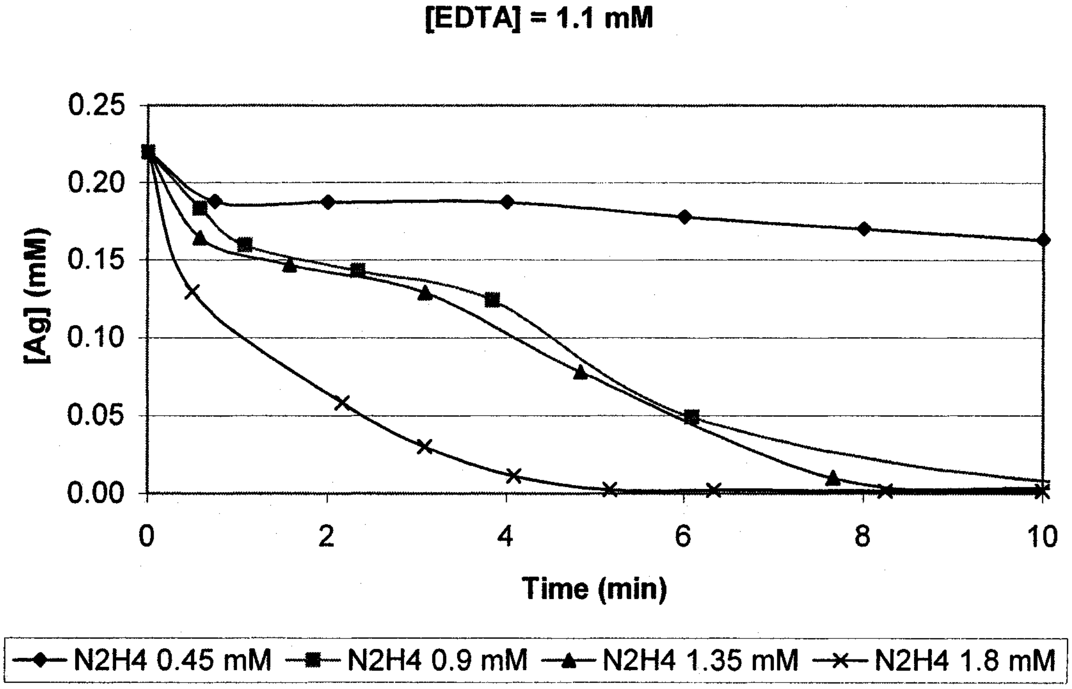

Figure 5.8: Effect of hydrazine concentration on the silver reduction rate

Even at various hydrazine concentrations the previously observed pattern keeps appearing. The variation of the hydrazine initial concentration brings about a modification of the characteristic values of the three reduction stages in terms of their length and slope. However, for the largest excess of hydrazine (1.8 mM), 32 times the stoichiometric amount, the silver reduction rate appears to occur in a smoother fashion and the three stage pattern is not found. In contrast, at a very low hydrazine concentration it is observed that the reaction does not take place to a great extent. In this case it seems that the second stage of the reaction, in which silver concentration remains roughly constant, becomes a very long one. It is important to mention here that even though this is the lowest hydrazine concentration used, there is an eight times excess with respect to the silver concentration, assuming a four to one silver to hydrazine stoichiometry.

The precipitation of silver was also carried out at a variety of silver concentrations, of 0.15 mM, 0.22 mM and 0.44 mM. Figure 5.9 shows typical results for EDTA and hydrazine concentrations of 2.2 mM and 1.1 mM respectively.

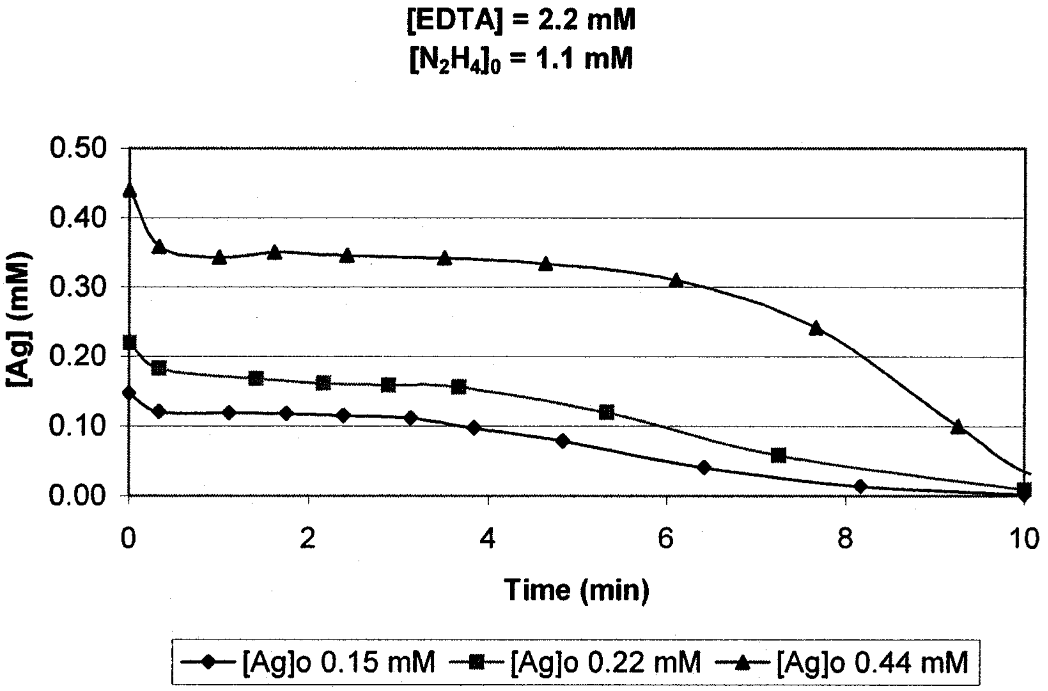

Figure 5.9: Effect of initial silver concentration on the reduction rate

Again the three stage behavior is observed. In order to clarify the effect of the silver concentration on the process, these results were normalized each with its own initial silver concentration (Figure 5.10).

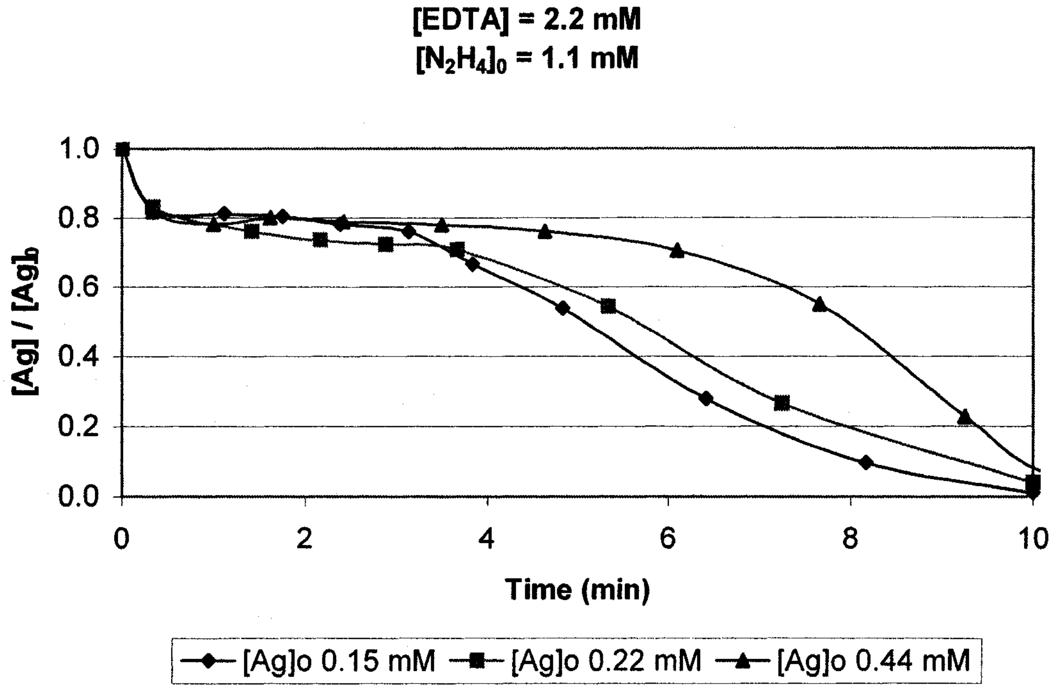

Figure 5.10: Effect of initial silver concentration on the reduction rate, normalized values

The most important aspect of this plot is that for all three normalized curves, the decrease of normalized silver concentration in the first stage of the reaction is about the same. This effect will be further studied and explained in section 5.4.1.

5.3 Interpretation of typical profile observed in the reduction rate

In this section, an attempt to explain the three stages observed in the reduction of silver is made. In order to explain the pattern, the analysis of the silver concentration profile was done by parts, and not as a whole.

5.3.1 Initial silver concentration decay

The initial fast decrease in silver concentration takes place within the first thirty seconds of the reaction. Indeed, it is possible that this initial precipitation takes place instantly. As the first sample is taken after thirty seconds, the results will be the same if the initial precipitation takes place instantly or along the first half minute of the experiment. There are two possible explanations for this initial silver concentration decrease. The first is related to the method of addition of the hydrazine. The second one is associated with the equilibrium of the silver – EDTA complex with the free silver.

First, the possibility of an initial decay as a result of the method of addition was considered. In the experiments shown the hydrazine concentration in the reaction mixture varied from 0.44 mM to 1.8 mM. However, the hydrazine solution added at the start of the experiment to the silver – EDTA – buffer mixture had a concentration of 10 mM. Thus, when adding the hydrazine, the first contact zones of the hydrazine solution with the silver-EDTA solution may have an excessively high concentration of the reducing agent. These high hydrazine concentration zones are likely to have a strong effect on the observed reaction rate. Indeed, as shown in Figure 5.8, for a high hydrazine concentration even in the presence of EDTA the reduction of silver takes place at a very high rate. This way, in these zones the silver present may be reduced at a very fast rate consequently giving as a result the high rate in the initial decrease of silver concentration. Once the silver and hydrazine solutions are thoroughly mixed, the hydrazine is diluted and the reaction rate is considerably slowed down.

Three experiments were carried out modifying the method of addition of hydrazine along with a blank experiment carried out under the normal procedure. If the formation of high hydrazine concentration zones causes the initial precipitation of silver, the modification of the method of addition will bring about variations on the observed precipitation kinetics.

For the first experiment, the pH was set at a value of 10 by the addition of ammonium hydroxide. It was shown in section 5.2.1 that at this pH, the precipitation of silver under the presence of EDTA does not take place. After two minutes, when the solution has been well mixed and therefore no high hydrazine concentration zones are present, acetic acid was added in order to reduce the pH down to seven, at which the reaction takes place at a slow rate. The time of the addition of acetic acid was set as time zero. The results obtained are shown in Figure 5.11.

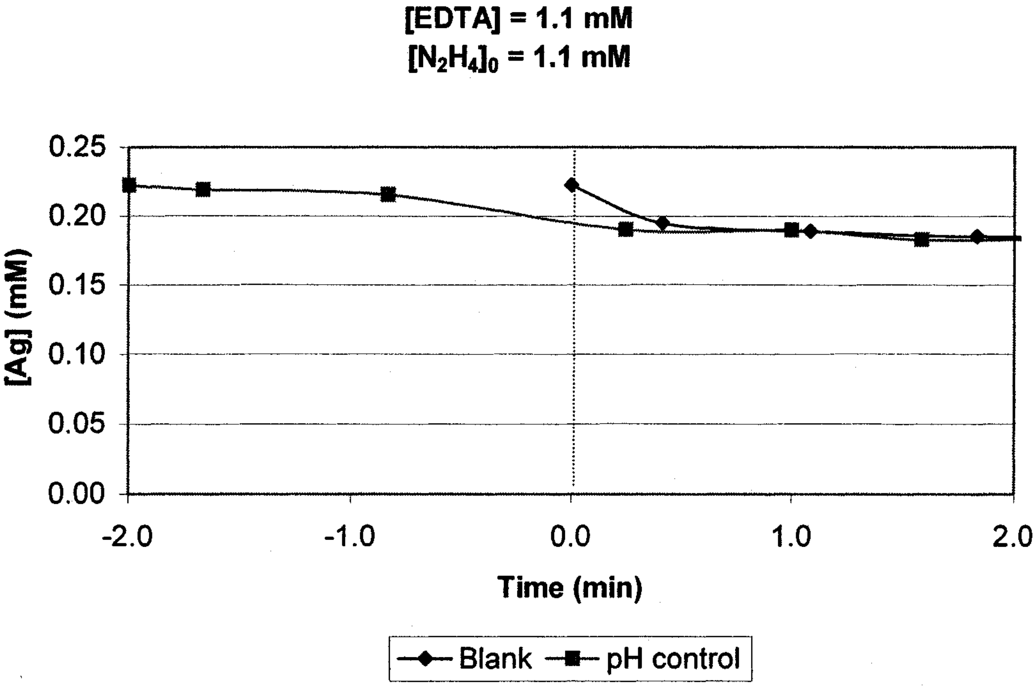

Figure 5.11: Effect of pH control on the initial silver decay

In the second experiment, hydrazine was added to the solution at rate of 1 mL/min, so it took almost one minute to add the total amount of hydrazine. Normally, the addition of hydrazine to the silver – EDTA solution takes about five seconds. This was expected to have an effect on the initial decay of silver concentration.

Finally, hydrazine was added at a concentration of 2 mmol/L, instead of 10 mmol/L used in the standard procedure. The results obtained from these two last experiments and the blank are shown in Figure 5.12.

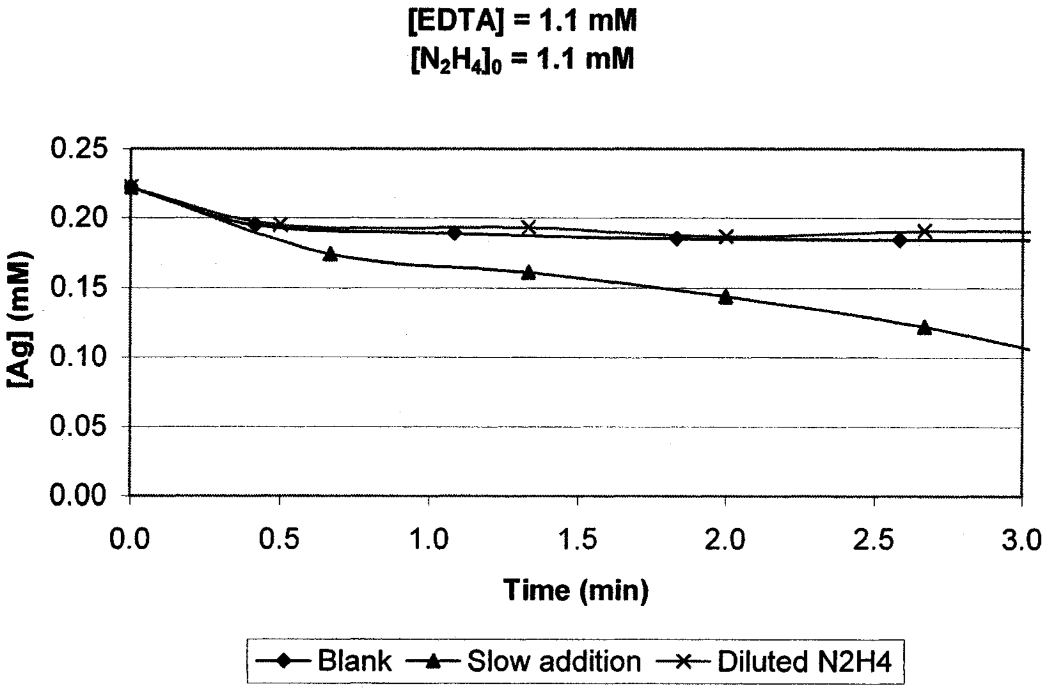

Figure 5.12: Effect of variation of the method of addition of hydrazine on the initial silver decay

As seen in these Figures 5.11 and Figure 5.12, the variation of the method of addition of hydrazine does not affect the initial decay of silver, with the exception of the slow addition. The usage of several methods of addition guarantees a difference in the formation of high hydrazine concentration zones. In the case of the pH control, there is no formation of high concentration zones because by the time at which the reaction is triggered by the addition of acid, the hydrazine and silver solutions are well mixed. In the case of the slow addition of hydrazine, after a fraction of the reducing agent has been added, silver particles are already formed. These particles have the effect of seeds on the reaction mixture. In a typical crystallization process, the seeds bring about an increase in the crystallization rate.

Further verification was attained with experiments ran at different mixing speeds. In case that there is a formation of high concentration zones, different mixing speeds are expected to produce variations in the results. The experimental data obtained is shown in figure 5.13.

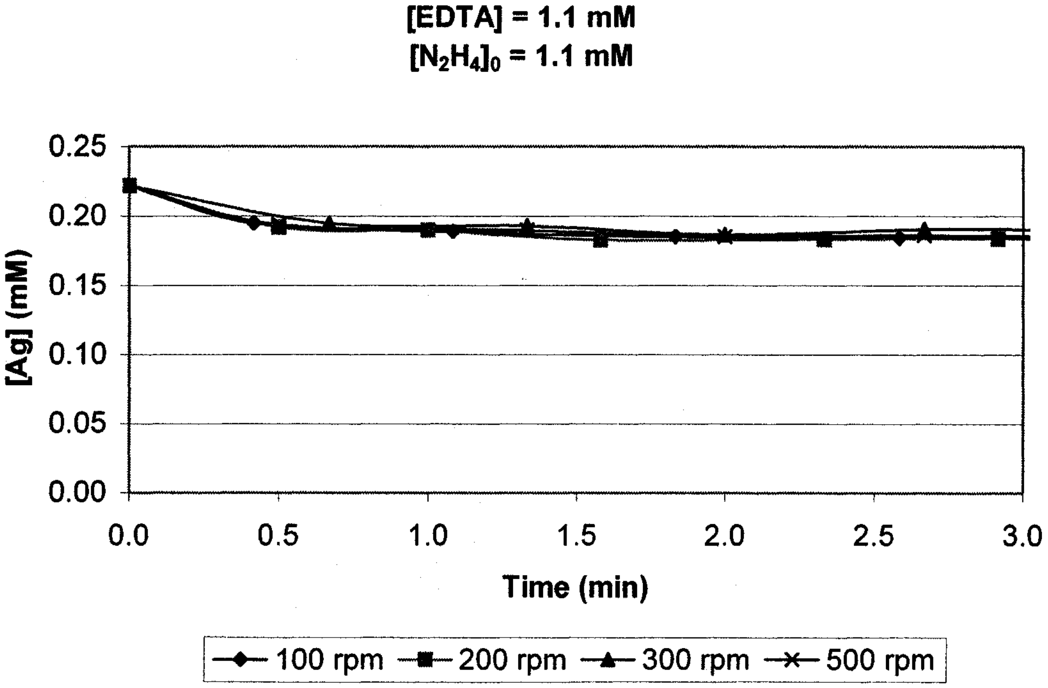

Figure 5.13: Effect of the mixing speed on the initial silver decay

As seen on figure 5.13, the speed of mixing in the solution does not bring about a change in the initial decay of silver concentration. This confirms that this initial decay is not a result of the formation of high hydrazine concentration zones.

The second possible explanation for the fast initial decay of silver concentration is the equilibrium between the silver – EDTA complex and the free silver. At equilibrium, the EDTA – silver complex coexists with free silver ions as well as unbound EDTA. As the reduction of silver with hydrazine takes place instantly, these free silver ions react with the hydrazine at the moment it is added. Therefore, the initial decay in the silver concentration may be due to the presence and immediate reduction of free silver ions present in the EDTA – silver equilibrium. Experiments were designed and carried out in order to test this hypothesis.

At equilibrium, the concentrations of each of the species (free silver ions, EDTA, silver – EDTA complex) are determined by both the initial concentrations of silver nitrate and EDTA and the equilibrium constant. This constant can be a function itself of the ionic strength of the solution and its pH, as well as of the temperature. However, as the experiments are carried out at similar ionic strengths, constant temperature, and at pH of seven, no change in the equilibrium constant is expected.

The equilibrium constant for the silver – EDTA complex can be calculated if the equilibrium concentrations of the free silver, EDTA and the EDTA – silver complex are known. The free silver concentration can be estimated from the amount that is reduced during this initial stage. Knowing this value and the initial EDTA and silver concentrations, an apparent equilibrium constant may be calculated. If this constant remains as such for several experiments at different concentrations, we can safely assume that indeed the equilibrium is the cause of the initial silver concentration decay. Experiments were run at different EDTA concentrations in order to try this. The results are shown in figure 5.14.

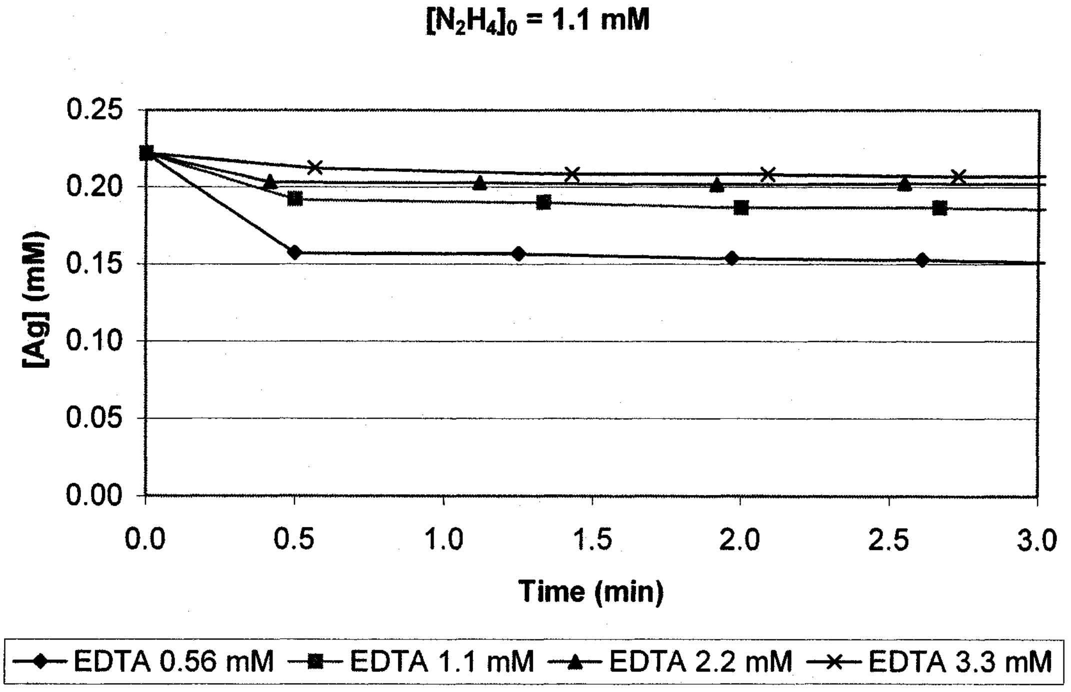

Figure 5.14: Effect of EDTA concentration in complex equilibrium

With the data obtained from the experiments, the apparent equilibrium constant was calculated for each case. An example of this calculations is given at the Appendix A. The results are presented in the following table.

Table 5.1: Apparent equilibrium constants for several EDTA values

EDTA (mM)	K x 10^{-3} (M^{-1})
0.56	5.65
1.1	5.96
2.2	5.07
3.3	4.98
Published value (Saran et al., 1995)	19.3

As Table 5.1 shows, for a variety of EDTA concentrations the value obtained for the equilibrium constant is about the same. This suggests that the hypothesis that the equilibrium of the silver – EDTA complex with its uncomplexed species is the cause of the initial decay of silver concentration. Even when published data present a value of four times the value obtained, it is not specified under which pH was this constant obtained. As shown in section 5.2.2, the pH is a major factor for the strength of the EDTA – silver complex.

5.3.2 Semi constant period and final decay of silver concentration

A period of an apparent slow rate of reduction (second stage in the reaction) and the sudden acceleration of this rate (third and final stage of the reduction) form part of the pattern observed in the decrease of silver concentration caused by the reduction with hydrazine in presence of EDTA. It should be noted that the silver and hydrazine concentrations at the beginning and end of the quasi stable stage, when the reaction seems to slow down and then be triggered again, are very similar. As an example of this, the silver concentration variations of the experiments presented in Figure 5.9 are of 5.6, 5.2 and 2.0% of the initial silver concentration in over three minutes. Also the EDTA concentration and pH are kept constant. Based on all this, there is no clear explanation based on the reduction kinetics to the stage behavior of the reaction.

A possible explanation for the presence of the plateau and final decay in silver concentration is based on the crystallization kinetics. As mentioned in the Introduction, crystallization consists mainly of three steps: nucleation, growth and agglomeration. In the case that the silver reduced goes mainly towards the nucleation process, the nuclei produced will go through the filter, which has a pore size of 0.1 microns (100 nm). Even after the nuclei have grown and agglomerated to a certain extent, these silver particles may still be smaller than the mentioned pore size. Since the Induced Coupled Plasma used for the determination of silver concentration may detect these silver nanoparticles, as mentioned in section 3.3, and account them for the total silver concentration, a decrease in the silver concentration will not be observed until the silver particles reach by growth and agglomeration a size similar to or larger than that of the filter pores. Before particles achieve this size, the observed silver concentration will remain almost constant, and once particles have reached this size the final silver concentration decay (third step in the three step pattern) will be observed. In order to test this hypothesis, several experiments were carried out.

First, the experiments showed in section 4.4 concerning the use of filters with different pore sizes were carried out. With these, the interference of reduced solid silver particles smaller than the filter pore size with the observed silver analysis was shown. This suggests the possibility that the observed three step silver concentration decrease, corresponding to the silver ions plus uncharged silver nanoparticles, is different to the actual soluble silver concentration profile. In order to verify this, experiments in which an attempt was made to control the crystallization kinetics were carried out.

The solubility of elemental uncharged silver is extremely low. Therefore, it can be safely assumed that all silver that is reduced to its elemental form either is converted into new nuclei or takes part in the growth process. Because of this the sum of the nucleation and growth rates is equal to the real reduction rate. In the present case, it is desired that all the elemental silver remains in particles larger than 0.1 microns. For this, no new nuclei are desired, so it is required to maximize the amount of reduced silver atoms that are incorporated into particles by the growth process. If these particles are already close to or larger than 0.1 microns, all the reduced silver may be determined by the available analytical methods.

This can be achieved by the maximization of the surface area available for growth. Experimentally, this is accomplished by seeding the reactive solutions. A set of experiments was carried out to verify this hypothesis. The seeds used were produced by silver reduction in the absence of a complexing agent, in order to guarantee that all the seeds were larger than 0.1 microns. The seed concentrations varied from 2.2 x 10^{-3} mM to 1.07 mM in all experiments where the initial silver, hydrazine and EDTA concentrations were 0.22 mM, 1.1 mM and 3.3 mM respectively. Figure 5.15 shows the results obtained.

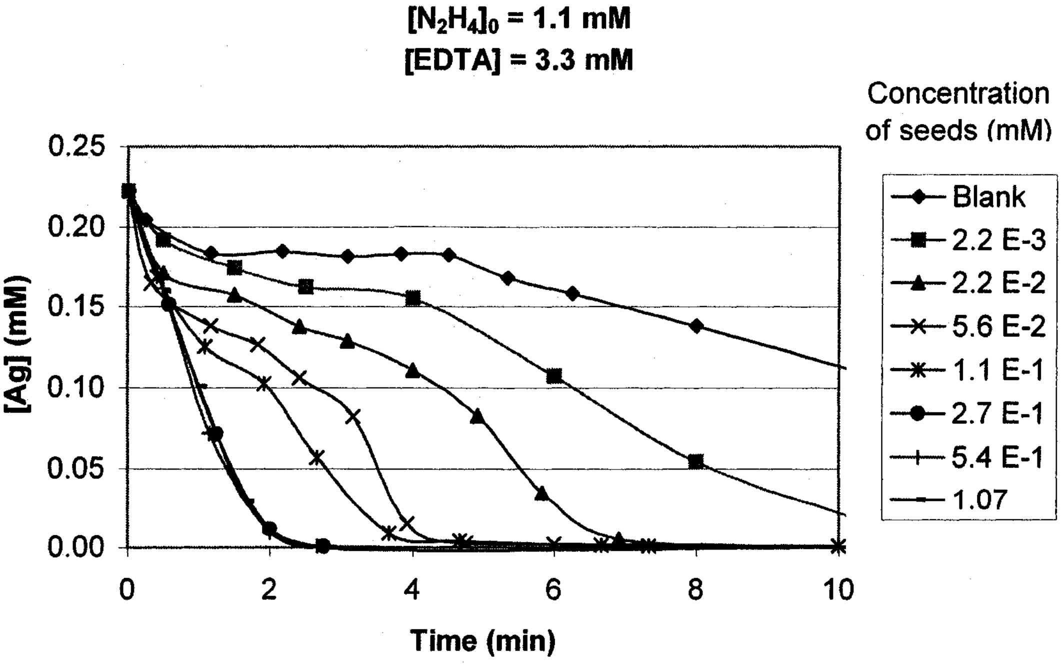

Figure 5.15: Effect of seeding on the observed rate of the reaction

The first observation is that seeding accelerates the observed rate of reaction. The addition of seeds to the reactive mixture results in the disappearance of the three stage behavior previously observed in the silver precipitation under the presence of EDTA. However, the most important observation is that for the three largest seed concentrations, 0.27 mM, 0.54 mM and 1.07 mM, the silver concentration decrease observed is exactly the same.

It has been mentioned that the addition of seeds promotes growth rather than nucleation. Also, the heterogeneous nucleation is favored over homogeneous nucleation. The minimization of homogeneous nucleation finds a limit when its rate becomes zero. The addition of larger amounts of silver crystals will have no effect on both the nucleation and growth rates, and therefore neither on the observed reaction rate. At this point, the observed reaction rate becomes equal to the particle growth rate plus the heterogeneous nucleation rate. As the homogeneous nucleation rate is equal to zero, the observed reaction rate is actually equal to the real silver reduction rate. As Figure 5.15 presents three consecutive concentrations (0.27 mM, 0.54 mM and 1.07 mM) which present exactly the same behavior, it can be assumed that such a point has been reached.

It is important to recall here the experiments in absence of a complexing agent. Even when the reaction rate observed in figure 5.15 is a fast rate, and the reaction proceeds to completion within the first two minutes, the reaction time is enough to take at least a couple of samples before completion. When compared to the reduction rate in the absence of EDTA (Fig. 4.2, 4.3), it is realized that the addition of the complexing agent effectively slows down the reaction.

5.4 Determination of Silver Reduction Kinetics

Since a method was developed to minimize the homogeneous nucleation in the precipitation of silver powders, it is possible to measure the soluble silver concentration, which includes both the silver ions and the silver present in the EDTA – silver complex. This allows the determination of the reaction kinetics.

Two sets of experiments were carried out in order to achieve this. In the first set, the initial hydrazine concentrations were set at 0.22, 0.44 and 1.11 mM while the EDTA concentration was kept constant at 2.22 mM for all experiments. In the second series, the initial hydrazine concentration was set at 1.11 mM and the EDTA concentrations were fixed at 2.22, 4.44 and 6.67 mM. The rest of the parameters were not varied, these being an initial silver concentration of 0.22 mM, pH 7 and a temperature of 21°C. The reactant concentrations used imply a stoichiometric excess of hydrazine of four, eight and twenty times, and of EDTA of ten, twenty and thirty times.

In order to promote growth and agglomeration, avoiding nucleation, seeds were added at a concentration of 0.36 mM. This concentration was chosen because as it was shown in section 5.5, at a seed concentration of 0.27 mM or higher the crystal nucleation is minimized. Figures 5.16 and 5.17 show respectively the effect of the hydrazine and EDTA initial concentrations on the actual silver reduction rate.

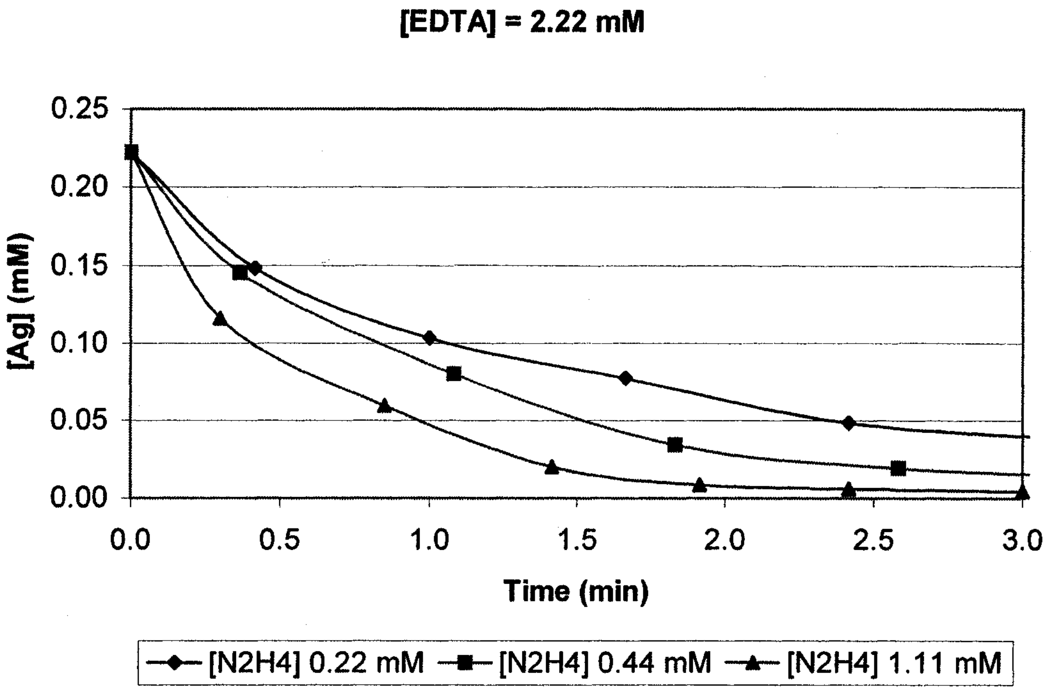

Figure 5.16: Effect of hydrazine concentration on actual reaction rate, seeding 0.36 mM

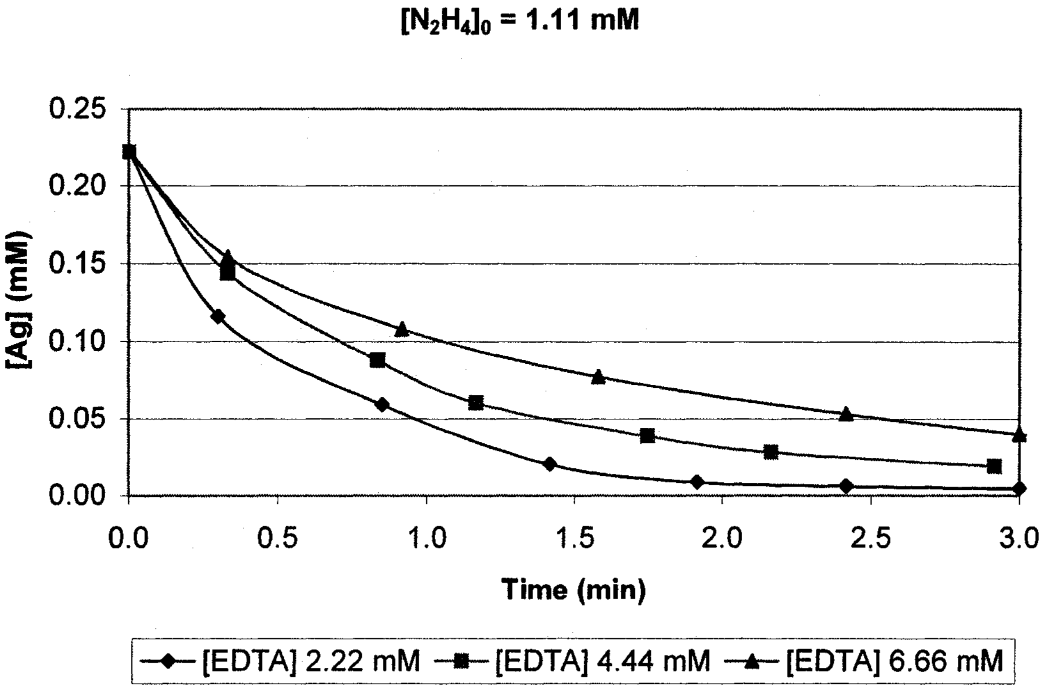

Figure 5.17: Effect of EDTA concentration on actual reaction rate, seeding 0.36 mM

Once the crystallization kinetics have been controlled, the experimental conditions do not allow silver nanoparticles to affect the determination of non reduced silver concentration, the characteristic three stage behavior is not observed at any silver, hydrazine or EDTA concentration. Also, the rate of reduction shows a clear decrease along with the silver concentration, as would be expected. As for the other reactant concentration effects, Figure 5.16 shows that as the initial hydrazine concentration increases, there is also an increase in the rate of reaction. On the other hand, an increase in the rate of reduction is observed along with a decrease of EDTA concentration in Figure 5.17. These relations between the reactant concentrations and the rate of reduction were the expected ones.

In order to correlate the experimental conditions to the rate of the reaction, the experimental data were adjusted to a function of the form:

$$r_{Ag} = k\,[Ag]^{\alpha}\,[N_2H_4]^{\beta}\,[EDTA]^{\gamma} \qquad 5.3$$

At a large excess of hydrazine and EDTA, it can be assumed that these reactant concentrations remain constant throughout the experiments. Thus, these variables can be grouped with the rate constant giving the following equation:

$$r_{Ag} = k'\,[Ag]^{\alpha} \qquad 5.4$$

The design equation for this simple batch reactor is:

$$d\,[Ag] / dt = -\,r_{Ag} \qquad 5.5$$

By combination of equations 5.4 and 5.5 and integrating and evaluating from time equal zero to t and from an initial silver concentration $[Ag]_o$ to $[Ag]$, equation 5.6 is obtained.

$$[Ag]^{-(\alpha-1)} = k'\,(\alpha-1)\,t + [Ag]_o^{-(\alpha-1)} \qquad 5.6$$

The data obtained from each of the experiments at a large excess of hydrazine was adjusted to a straight line according to equation 5.6. This way, the order of the reaction with respect to silver (α) was calculated. Subsequently, the logarithm of the apparent reaction constants (k') were linearized in order to obtain the order of the reaction for the hydrazine and EDTA concentrations. This was done according to equations 5.6 and 5.7.

$$k' = k\,[N_2H_4]^{\beta}\,[EDTA]^{\gamma} \qquad 5.7$$

$$\ln k' = \ln k + \beta \ln [N_2H_4] + \gamma \ln [EDTA] \qquad 5.8$$

The parameters for the equation of the rate of reduction of silver obtained are the following.

$$r_{Ag} = k\,[Ag]^{\alpha}\,[N_2H_4]^{\beta}\,[EDTA]^{\gamma} \qquad 5.3$$

with $k = 9.3537$ [milimoles per liter]$^{0.08}$ per minute

$\alpha = 1.31$

$\beta = 0.72$

$\gamma = -1.11$

It is important to notice that the silver concentration used for the determination of the reaction kinetics is not the silver ion concentration, but the total soluble silver concentration. This includes the one present in the EDTA – Silver complex. Similarly, the EDTA concentration includes both the free EDTA and the EDTA – Silver complex. Therefore, for future purposes, these concentrations are the ones that must be used in order for the equation presented to be valid.

A comparison of theoretical values obtained with the given equation and experimental data is presented in Figure 5.18 and Figure 5.19.

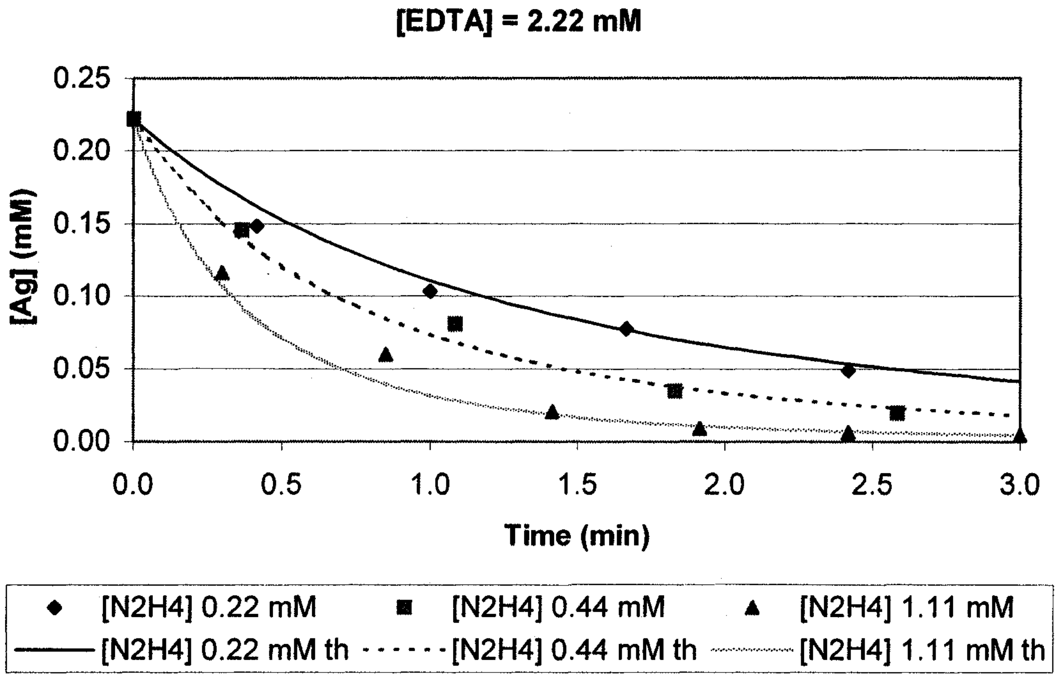

Figure 5.18: Effect of hydrazine concentration on silver reduction; theoretical and experimental values

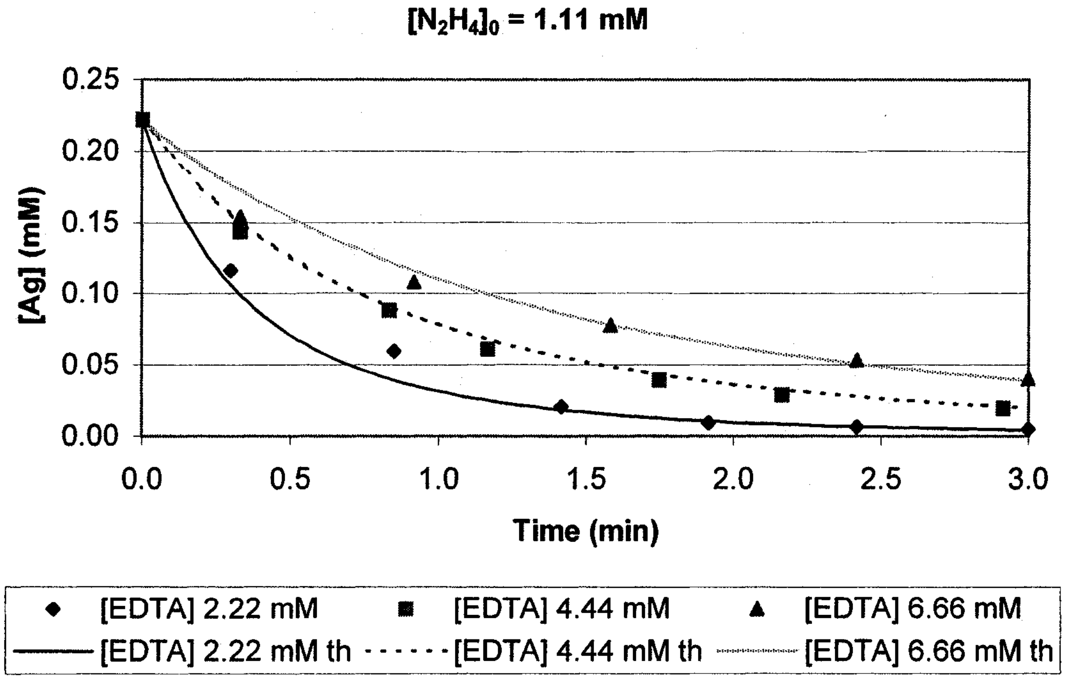

Figure 5.19: Effect of EDTA concentration on silver reduction, theoretical and experimental values

Figures 5.18 and 5.19 compare the experimental data with theoretical curves obtained by the integration of the reaction rate calculated. As expected, the experimental and theoretical data present very close values. Nevertheless, further validation of this equation is needed in the next stages of the global project.

With the reaction kinetics determined, it is possible for the project to proceed to the modeling phase.

5.5 Corroboration of silver precipitation behavior with SEM pictures

It has been stated that at the early stages of the reaction very small silver particles, in the nanometer range, precipitate. These initial particles cannot be retained by the filter and are therefore detected by the induced coupled plasma analysis. As the experiments proceed, these silver crystals grow and agglomerate, resulting in larger crystals which are retained by the filter and cause the final drop of silver concentration. This mechanism was already tested experimentally, however, in order to further verify these assumptions, pictures of silver particles were taken in a scanning electron microscope.

The precipitation of silver particles was carried out both under the presence and absence of EDTA. Samples were taken at different reaction times, taking a drop of the suspension and evaporating it, leaving only the silver particles plus the new crystals of other species present. The presence of silver particles was determined both visually and by using an X-ray diffractometer. Figure 5.20 shows a SEM picture of silver powders precipitated in absence of EDTA or any other complexing agent.

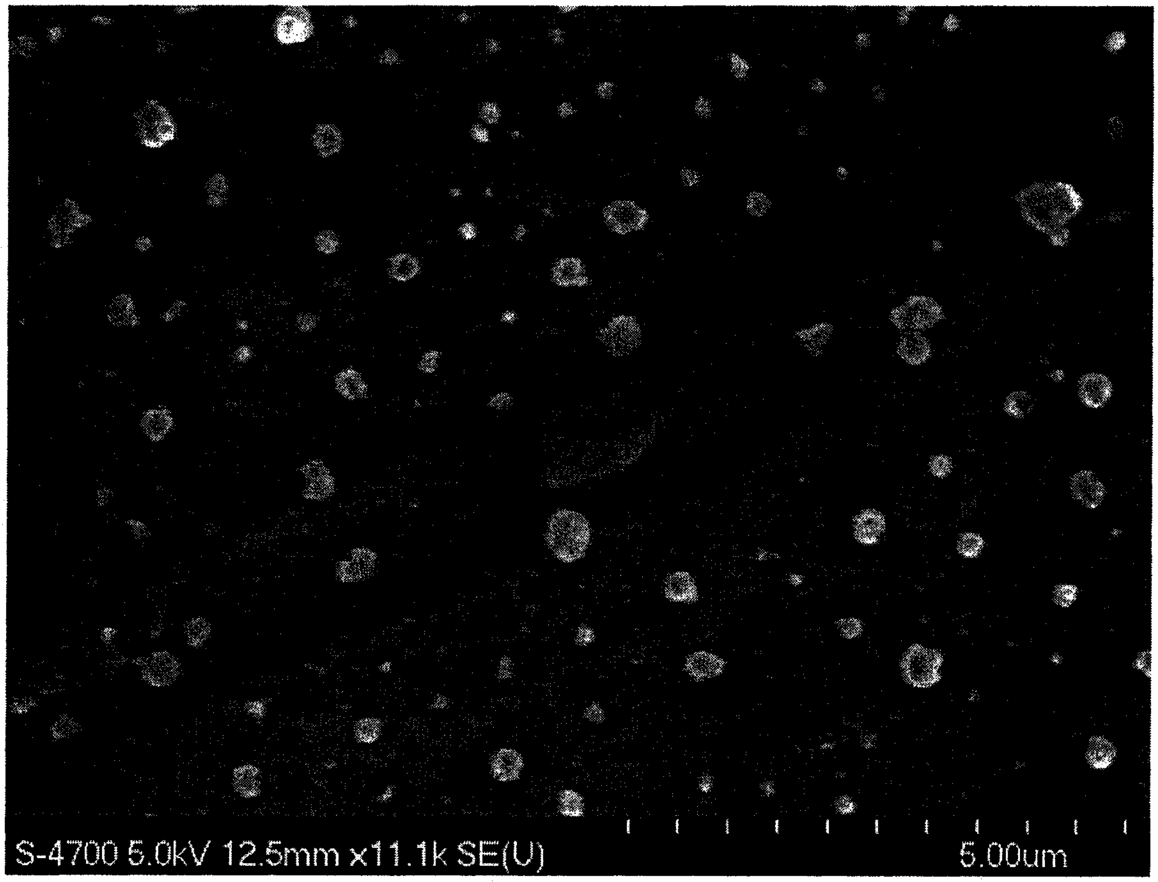

Figure 5.20: Silver particles produced without EDTA, magnified 11100 x

The sample prepared for this picture was taken one minute after adding the hydrazine. At this time the silver reduction has taken place to a full extent. As can be observed, silver particles are well distributed along the plate, but a closer look is needed to determine their size. In figure 5.20, a certain roughness can be observed in the background. This is just an effect of the aluminum plate on top of which the sample was prepared, and will be observed along all the pictures to some extent.

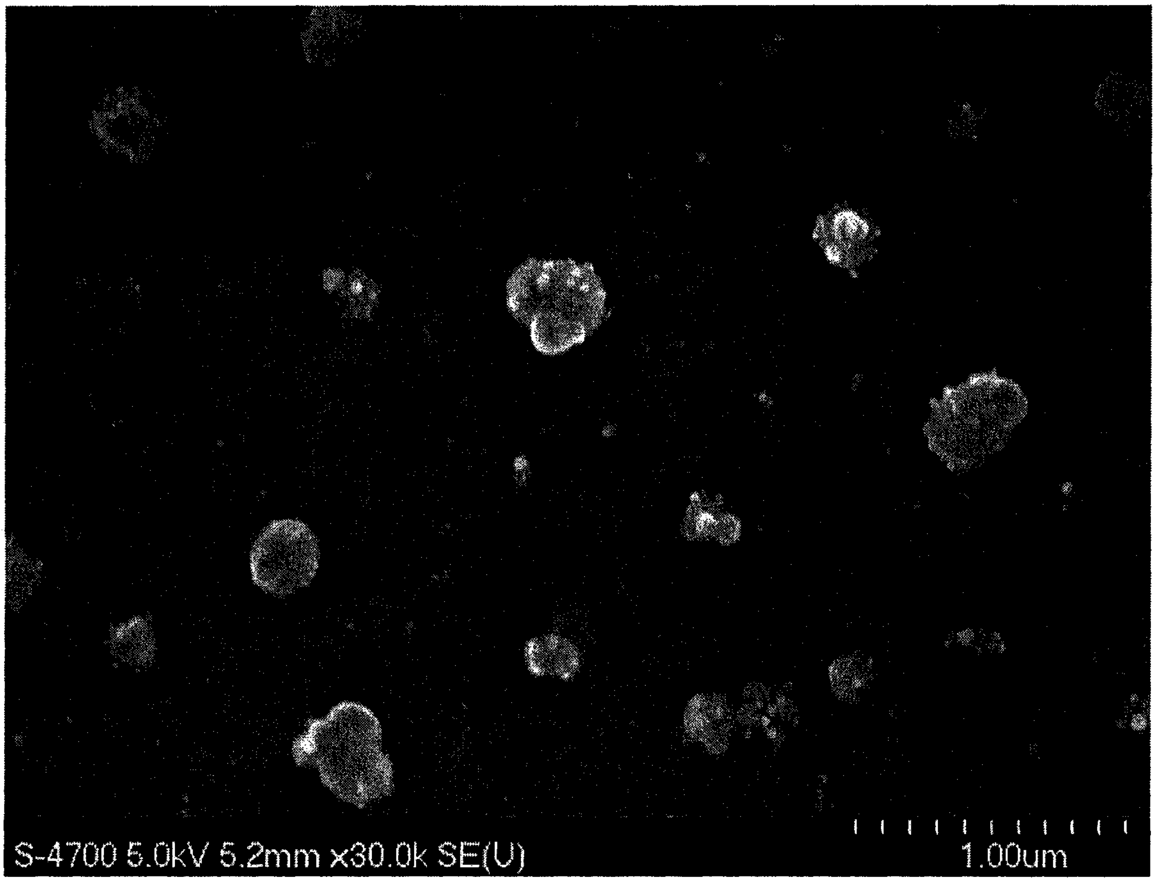

Figure 5.21: Silver particles produced without EDTA, 30000 x magnification

This picture allows the distinction of silver particles into two groups. The most notable one is that of the larger silver particles, which have diameters of more than 0.1 microns. When filtering, these particles will be retained by the filter and therefore will not be quantified in the analysis. On the other hand, very small silver particles can also be seen in this picture. These particles look almost like white dots on the picture, and are much smaller than the filter pore size. It can be stated from figure 5.21 that there is a much larger number of particles smaller than the filter pore size in relation to the particles that must be retained by the filter. However, there is not a big effect of these particles on the silver concentration due to the fact that the largest mass of silver is concentrated in the larger particles.

It is also important to notice the small bumps on the surface of the particles larger than one micron. These are smaller particles agglomerated into these larger ones. The morphology of the particles observed exposes that agglomeration is indeed an important step in the kinetics of silver precipitation.

Particles produced under the presence of EDTA were also observed under the microscope. Figure 5.22 shows a picture of a sample taken forty seconds after the addition of the hydrazine. At this time, the initial decay of silver concentration due to the silver-EDTA equilibrium has taken place, and the apparent silver concentration shows a constant behavior.

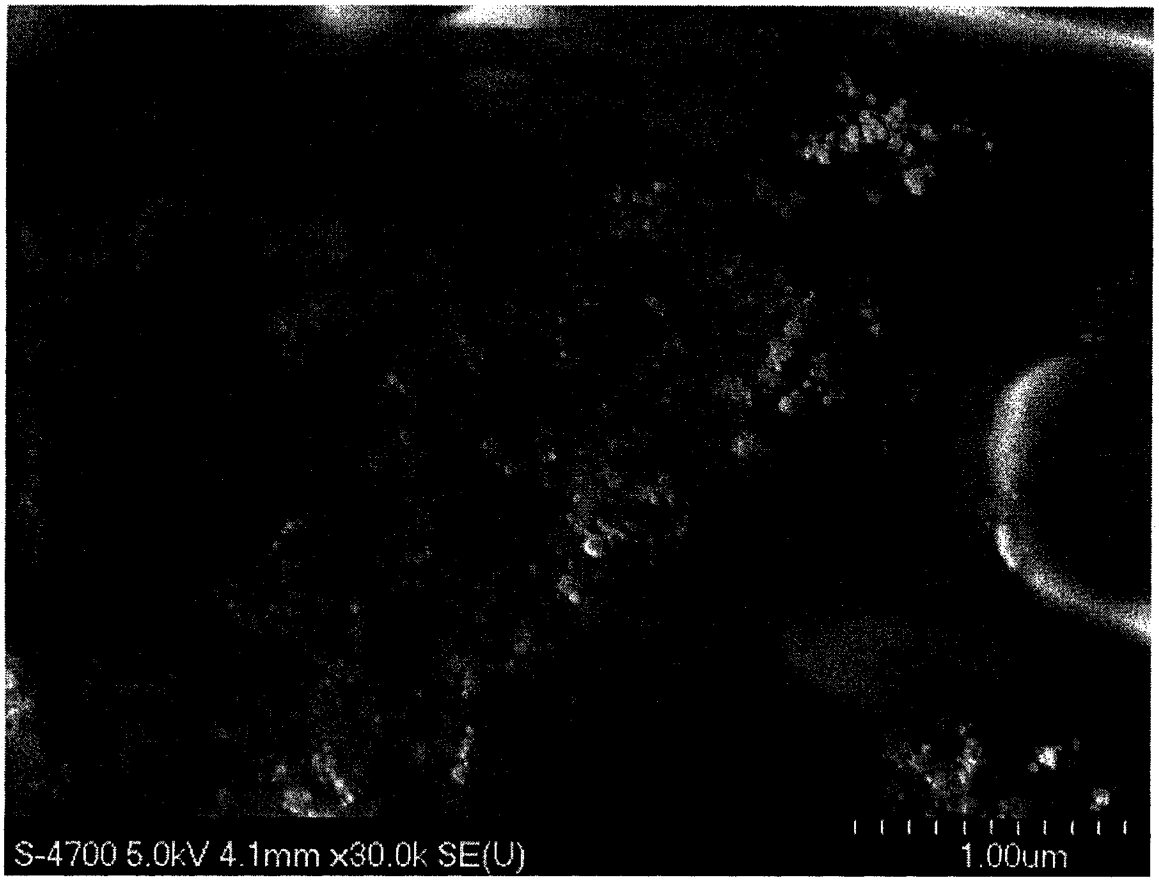

Figure 5.22: Silver particles produced with EDTA, 30000 x magnification

A large amount of silver particles with a diameter of les than 100 nanometers is observed. At the time this sample was taken, the reduction of silver was expected to be on its way, precipitating particles smaller than the filter size. The observations from the SEM picture are consistent with this theory, having very few or no silver particles larger than or close to the 0.1 micron filter pore size.

A sample was taken in the same experiment, only this was taken after thirteen minutes. At this time, the final observed silver concentration decrease has taken place. Figure 5.23 shows a picture of this sample.

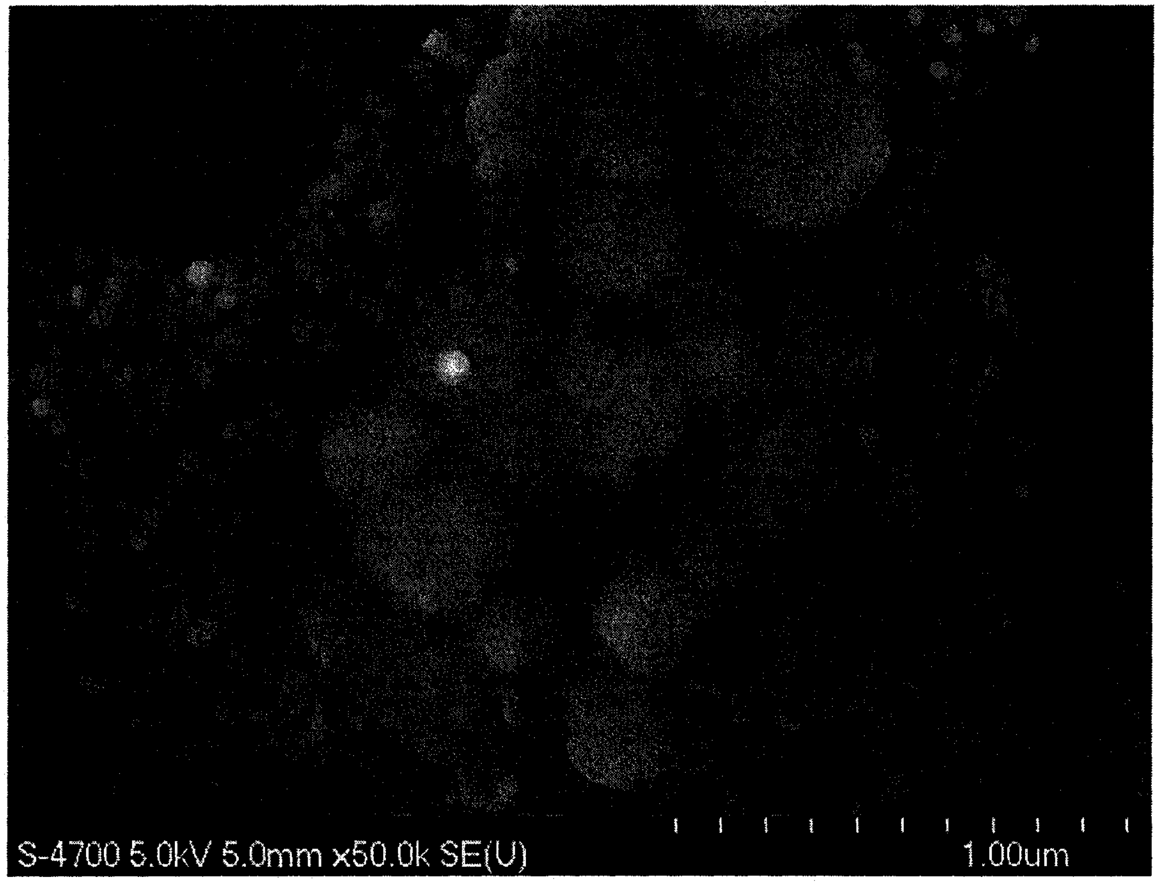

Figure 5.23: Silver particles produced under the presence of EDTA after final observed silver concentration decrease, 30000 x magnification

At the time this picture was taken, the silver conversion observed was about 90%, therefore an observation of particles larger than 0.1 microns, along with some others slightly smaller than this pore size is expected. Effectively, two groups of silver particles are observed in this picture. On one hand, particles larger than 0.1 microns appear, which must be retained by the filter of pore size 0.1 micron. Also particles of diameters slightly lower than 0.1 microns are observed. Even when these smaller particles can make their way through the filter, they show particle diameters larger than those observed at the beginning of the reaction. This behavior is consistent with the experimental observations.

Also in figure 5.23, it is observed that particles are not well dispersed in the plate. This suggests the possibility of agglomeration, which would also keep the particles from passing through the filter and therefore bring about the final decay of silver concentration.

CHAPTER 6. Conclusions and Future Work

The following conclusions were obtained from the experimental work and the analysis of the data obtained.

- The reduction of silver with hydrazine without the presence of a complexing agent takes place at too fast a rate to be evaluated experimentally, even at very low reactant concentrations and temperature.

- The selection of an adequate complexing agent is critical for the control of the reduction of silver nitrate with hydrazine. In the event that the complex formed with silver is too strong, the reaction will take place at an extremely slow rate. On the other hand, if the complexing agent is too weak, the reaction takes place within the first 20 seconds.

- Ethylene diamine tetraacetic acid can be an effective complexing agent for the silver reduction with hydrazine, depending on the conditions, mainly pH, at which the reaction is carried out. At pH of seven, the optimum one for our purposes, the silver reacts with hydrazine at a one to two ratio.

- Seeding accelerates the apparent reaction rate by promoting the crystal growth instead of the nucleation. By reaching a given value of seeds in the suspension, the apparent reaction rate turns to be equal to the growth rate and the real reduction rate. This way, the reaction rate can be evaluated in order to be expressed as a function of the reactant concentrations.

- The reduction of silver with hydrazine in presence of EDTA takes place at a rate of order 1.31 with respect to silver, 0.72 with respect to hydrazine, and –1.11 with respect to EDTA, with a rate constant of 9.35.

Based on these conclusions, the next steps of the project can be defined. Some of the tasks to be done in order to achieve the control of the silver particle properties by the manipulation of the reactant concentrations are the following.

- The corroboration of the reduction rate equation obtained in Section 5.4 under several reactant concentrations.
- The evaluation of experimental particle size distributions produced at a variety of concentrations.
- The development of a model of silver precipitation contemplating reaction, nucleation, growth and agglomeration rates.
- The determination of the physical parameters related to the crystallization rates by the comparison of the model and experimental results.

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Appendix A

Apparent equilibrium constants were calculated based on the reaction of formation of the 1:1 silver-EDTA complex, shown in equation A.1.

$$Ag^+ + Y^{4-} \longleftrightarrow AgY^{3-} \qquad \text{A.1}$$

For this reaction, the equilibrium constant is defined as follows:

$$K_{eq} = \frac{a_{AgY^{3-}}}{a_{Ag^+}\ a_{Y^{4-}}} \qquad \text{A.2}$$

Evaluating the activities at equilibrium.

As the experiments were carried out at low concentrations, we can assume that the solutions are ideal and the activity coefficients are equal to one. Therefore, the activities are equal to the concentrations of the respective species. The equation of the equilibrium constant remains as following:

$$K_{eq} = \frac{[AgY^{3-}]}{[Ag^+]\ [Y^{4-}]} \qquad \text{A.3}$$

Once again, evaluating the concentrations of all species at equilibrium.

The apparent equilibrium constants were calculated assuming that the initial decrease of silver concentration was caused by the reaction of unbound silver with hydrazine. Based on this, the amount of silver in form of free ions can be calculated as the difference between the total silver concentration before the addition of hydrazine and the total silver concentration after the initial silver decay. Consequently, the concentration of silver-EDTA complex at equilibrium is equal to the total silver concentration after the initial decay. Finally, the free EDTA concentration at equilibrium is equal to the initial EDTA minus the silver-EDTA complex concentration.

The data for the experiment at an initial EDTA concentration of 1.1 mM is presented next along with the respective calculations.

Table A.1: Data for calculations of apparent equilibrium constant at EDTA initial concentration of 1.1 mM.

T (min)	Total Ag (mM)
0	0.222
0.5	0.188

With this data, the concentrations at equilibrium are calculated:

$[Ag^+]_{eq} = 0.222 \text{ mM} - 0.188 \text{ mM} = 0.034 \text{ mM}$

$[AgY^{3-}]_{eq} = 0.188 \text{ mM}$

$[Y^{4-}]_{eq} = 1.111 \text{ mM} - 0.188 \text{ mM} = 0.923 \text{ mM}$

$$K_{eq} = \frac{[AgY^{3-}]}{[Ag^+]\,[Y^{4-}]} = \frac{0.188 \text{ mM}}{(0.034 \text{ mM})\,(0.923 \text{ mM})} = 5.96 \text{ mM}^{-1} = 5.96 \times 10^3 \text{ M}^{-1}$$

$$\mathbf{K_{eq} = 5.96 \times 10^3\ M^{-1}}$$