Synthesis of gold nanoparticles stabilised by ionic liquids

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Abstract

In the present work we studied the effects of the alkyl chain length, anion nature and concentration of ionic liquids of Imidazolium family on the final properties of gold nanoparticles (AuNPs). For this study, we used ionic liquids of the 1-alkyl-3-methylimidazolium chloride and bromide series with the alkyl group length ranging from C_2 to C_{16} in concentrations of 10 to 200 mM. Their self-organisation in aqueous solutions and in the presence of a gold salt were investigated. The AuNPs are synthesised and studied by two ways of reduction, by chemical reduction with NaBH₄ and by X-ray irradiation.

In order to fully characterise the systems under study, we carried out UV-Visible spectroscopy, High Resolution Transmission Electron and Scanning Electron Microscopies and Small Angle X-ray Scattering. Thus we were able to extract information such as the size, size distribution, morphology and degree of aggregation of the gold nanoparticles in solution depending on the synthesis conditions.

Moreover we were able to demonstrate the influence of the ionic liquid nature on the final properties of the gold nanoparticles.
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1. Introduction

The study of metal nanoparticles has been an extremely active area in recent years because of their application in different fields of physics, chemistry, material science, medicine and biology, as a result of their unique electronic, optical, magnetic, mechanical, physical, chemical and catalytic properties. The intrinsic properties of metal nanoparticles are mainly determined by their size, shape, composition, stability, crystallinity, structure, etc. In principle, one could control any one of these parameters to fine-tune the properties of this nanoparticle.\textsuperscript{[1-3]} Therefore, there is increasing interest in the development of studies on the synthesis and stabilisation techniques for obtaining nanoparticles of controlled size and shape.

Gold nanoparticles (AuNPs) stand out among the other metal nanoparticles due to their greater stability and fascinating aspects such as assembly of multiple types involving material science, behaviour of the individual particles, size-related electronic, magnetic, optical properties, and applications to catalysis and biology.\textsuperscript{[4,5]} In addition, AuNPs are biocompatible\textsuperscript{[6]} and potential carriers for efficient cellular delivery of various drugs and bioactive molecules. Due to these aspects, AuNPs are one of the most useful and studied nanoparticles in industry and medicine.\textsuperscript{[1]}

However, nanoparticles are solely kinetically stable and they should be stabilised against aggregation.\textsuperscript{[1]} Thus, to obtain stable dispersions of AuNPs in solution, it is necessary to use stabilisation methods. The most common strategy of stabilisation is the use of protective agents that could offset the Van der Waals attractive forces through steric and electrostatic repulsions between adsorbed ions and counter-ions associated preventing the aggregation of nanoparticles.\textsuperscript{[7]}

Electrostatic stabilisation occurs by adsorption of ions to metallic surface leading to multi-layers, which results in Coulombic repulsive forces between individual particles. Steric stabilisation is achieved by involving the metal centre and a sterically bulky layer material, such as polymer or surfactant, to promote a
steric barrier preventing the approach of the metal centres. Some stabilisers combine both effects such as, for example, polyoxoanions.\[^7\] These stabilisation types are illustrated in Figure 1.

![Figure 1](image-url)

**Figure 1.** Scheme of stabilisations: electrostatic (a), steric (b) and electrosteric (c).\[^8\]

The synthetic methods allow the preparation of many types of water or organic solvent-soluble nanomaterials, such as uniform nanometer sized particles. Ionic liquids (ILs), in particular the 1-Alkyl-3-methylimidazolium, have recently been used as both “solvents” and stabilisers for the preparation of metal nanoparticles.\[^9\]

Ionic liquids (ILs) are a class of environmentally friendly compounds with melting points below 100 °C, that is, liquids composed of ions only. The reason behind this uncommon behaviour is the presence of the sterically mismatched ions that resist solid formation. These salts are characterised by weak interactions, owing to the combination of a large cation as the charged hydrophilic headgroup and one or more hydrophobic tails with a charge-delocalised anion. The ILs are currently used in several applications because of their extraordinary properties including nonvolatility, nonflammability, and high ionic conductivity. Other important properties are the ability to dissolve large number of organic, inorganic and polymeric materials in a wide temperature
range. A wide range of intermolecular interactions such as ionic bonding, hydrogen bonding, van der Waals, n−π and π−π interactions can give rise to different physical, chemical, and biological phenomena. Imidazolium ILs possess pre-organised structures through mainly hydrogen bonds that induce structural directionality, contrary to classical quaternary ammonium salts, in which the aggregates display charge-ordering structures. This structural organisation of ILs may be used as “entropic drivers” for spontaneous, well-defined, and extended ordering of nanoscale structures.

The intrinsic high charge of imidazolium salts, which creates an electrostatic colloid-type protection (DLVO-type stabilisation) for the transition-metal nanoparticles may be, at first approximation, adequate for the description of the stabilising effect. It is known that any structural and concentration of the ionic liquid variation may be reflected in the stability of the nanoparticles as well as their shape and size. Safavi and Zeinali showed a possible scheme of formation and that the stability of AuNPs depend directly on the concentration of the ionic liquid. They propose that the halide ions can be strongly adsorbed on the gold surface, creating a negatively charged layer and the corresponding hydrocarbon chains of the surfactant are ordered outward due to the electrostatic interaction of the surfactant positive head groups by the negative charges on AuNPs surface (Figure 2a). At low IL concentrations, IL’s cations, which interact with the adsorbed halide ions on the AuNP, surface can neutralise the particles charge. So the particles begin to aggregate in water (Figure 2b), and after several hours the aggregates precipitate from the solution. Upon addition of an excess of IL, more IL cations were able to attach to the nanoparticle’s surface by hydrophobic interaction between alkyl chains (Figure 2c). It follows stable AuNPs dispersion in the aqueous solution due to the positive charges on the particles’ surface, giving the particles a repulsive force as shown in Figure 2.
Figure 2. The mechanism of AuNPs formation by increasing ILs’ concentration.[2]

Hatayema and co-workers[19] showed the effects of varying the chain length of 1-alkyl-3-methylimidazolium tetrafluoroborate on the formation process of AuNPs by sputter deposition. They concluded that the surface tension influences the initial formation process of AuNPs on the surface of an ionic liquid, and the viscosity affects the aggregation process during the dispersion of the Au particles from the surface of the IL. They also highlighted the importance of studying the effect of the anion of the IL on the nanoparticle’s stability, as this forms the first layer of stabilisation due to its adsorption on the surface of the nanoparticle.

It is evident that the knowledge of the mechanisms of formation, the interactions of the ionic liquid with the nanoparticles, and how this leads to their stabilisation, without losing their catalytic properties, is crucial. In this work we have studied the effects of the variation of parameters such as the chain length, nature of the anion and the concentration of ILs of the imidazolium family on the formation of AuNPs and further understand the influence on their stability, size, shape and size distribution.

The second part of this work is focusing on comparing two methods of reducing the metal salt tetrachloroauric acid: 1) by chemical reduction NaBH₄ and 2) by X-ray irradiation. The study of the feasibility of reducing the gold by X-ray irradiation is very new and is presented as an alternative route to obtain
AuNPs quickly and without the use of chemical reagents, reducing the production of residues linked to the process.

For this study, all samples were characterized by UV-Vis spectroscopy which provides information related to the size and morphology of the gold nanoparticles by the position of the surface plasmon resonance peak. High Resolution Transmission Electronic Microscopy (HR-TEM) and Scanning Electronic Microscopy (SEM) were carried out to illustrate the shape, size and surface details of AuNPs. Small Angle X-ray Scattering (SAXS) measurements were performed to determine the size, shape and size distribution of all the gold nanoparticles in solution, and as well to study the IL structure and organisation in solution. Moreover in situ reduction of AuNPs by X-ray irradiation was carried out on the SAXS beamline.

2. Material and methods

2.1 Materials

Gold (III) chloride trihydrate (HAuCl₄·3H₂O) and sodium borohydride (NaBH₄) were obtained from Sigma-Aldrich. 1-Ethyl-3-methylimidazolium chloride (C₂mimCl), 1-Butyl-3-methylimidazolium chloride (C₄mimCl), 1-Hexyl-3-methylimidazolium chloride (C₆mimCl), 1-Decyl-3-methylimidazolium chloride (C₁₀mimCl), 1-Dodecyl-3-methylimidazolium chloride (C₁₂mimCl), 1-Hexadecyl-3-methylimidazolium chloride (C₁₆mimCl), 1-Hexyl-3-methylimidazolium bromide (C₆mimBr), 1-Decyl-3-methylimidazolium bromide (C₁₀mimBr), 1-Dodecyl-3-methylimidazolium bromide (C₁₂mimBr) were purchased from io-li-tec. All chemicals and reagents were acquired with highest purity and used without any further purification. Water used in all procedures was obtained from a water purification system (Purelab from ELGA) and had a measured resistivity of 18.2 MΩ cm⁻¹.

2.2 Synthesis of gold nanoparticles

To elucidate the effect of the alkyl chain length, nature of anion and concentration on the formation of AuNPs, we used ionic liquids with alkyl chain
length of C₂, C₄, C₆, C₁₀, C₁₂, C₁₆ for the chloride anion and C₆, C₁₀, C₁₂ for the bromide anion at the following concentrations: 10, 25, 50, 100 and 200 mM.

Gold nanoparticles (AuNPs) obtained by chemical reduction with agent NaBH₄ were prepared according to the following procedure. First, a volume of 0.84 mL of 6 mM HAuCl₄ solution was mixed with 1.66 mL of a solution of ionic liquid with subsequent addition of 2.50 mL of a solution of the reducing agent NaBH₄ with concentration of 10 mM, as illustrated in Figure 3. In the case of reduction by X-ray irradiation, the same procedure was followed, skipping the NaBH₄ step. Then the solutions were placed in the X-ray beam of the SAXS1 beamline for different exposure times.

![Figure 3](image.png)

**Figure 3.** Scheme of synthesis of gold nanoparticles by chemical reduction with NaBH₄.

### 2.3 Characterisation techniques

#### 2.3.1 UV-Vis Spectroscopy

Among the methods of characterisation of NPs, spectroscopy in the ultraviolet-visible (UV-Vis) region is one of the most simple and accessible as the electronic spectra of metal nanoparticles, such as Au and Pt, exhibits a sharp absorption in the visible region due to surface plasmon resonance, (SPR, λ_{spr} and A_{spr}). This absorption is not observed in macroscopic samples, because its origin is directly related to the collective motion of electrons on the surface of the nanoparticles, which is observed when an electromagnetic wave interacts with the nanoparticle causing a displacement of the electron cloud.²⁰,²¹
The colloidal dispersions of AuNPs which possess an intense red colour have smaller NPs than solutions which tend to dark blue colour. Dispersions exhibit dark coloration and formation of small agglomerates, a second band due to surface plasmon resonance can also be observed at longer wavelengths, i.e., the transition energy between bands is smaller with an increase in the density of electronic states. \cite{22,23}

Thus, the SPR peak can provide estimates of sizes of nanoparticles using the mathematical treatment proposed by Haiss and co-workers\cite{24}, which proposes that for particle diameters \((d)\) ranging from 35 to 100 nm it is calculated from the peak position according to equation \(1\).

\[
d = \frac{\ln\left(\frac{\lambda_{spr} - \lambda_0}{L_1}\right)}{L_2}
\]

For calculating are used fit parameters determined from the theoretical values for \(d > 25\) nm \((\lambda_0 = 512; L_1 = 6.53; L_2 = 0.0216)\) with error of only 3%. This equation cannot be used to determine the size of nanoparticles with diameter smaller than 35 nm. Since, for decreasing particle size, \(A_{spr}\) is increasingly damped relative to the absorbance at other wavelengths, the ratio of the absorbance at different wavelengths may be used to determine the particle size without knowledge of the concentration. For this case, the equation \(2\) that involves the ratio \(\left(\frac{A_{spr}}{A_{450}}\right)\) can be particularly suitable to calculate the particle diameter (in nm). The theoretical coefficient \((B1 = 3.55; B2 = 3.11)\) lead to a larger error of \(\sim 18\%\) while the experimentally determined fit parameters \((B1 = 3.00; B2 = 2.20)\) lead to an improved average deviation of \(\sim 11\%\).

\[
d = e^{\left(B_1 \frac{A_{spr}}{A_{450}} B_2\right)}
\]

UV-Visible spectroscopy (UV-Vis) was performed using an Agilent 8453 equipment operating in the 200-800 nm range for the characterisation of surface plasmon resonance (SPR) of the AuNPs. All measurements were carried out using the 1 mm path-length quartz cell.
2.3.2 High resolution transmission electronic microscopy

The high resolution transmission electronic microscopy (HR-TEM) micrographs of the AuNPs were obtained using a high resolution transmission electron microscope JEM-3010 URD operated at an accelerating voltage of 300 kV. Samples for HR-TEM were prepared by dissolution in isopropyl alcohol and placed a drop on a carbon-coated copper grid, dried at room temperature.

2.3.3 Scanning electron microscopy

The scanning electron microscopy was used to complement the information about the size and shape of nanoparticles and illustrate them. The SEM used was an Inspect F50. The samples were prepared in the same way as the HR-TEM samples.

Both measurements of HR-TEM and SEM were performed at the LNNano (Campinas, Brazil).

2.3.4 Small angle X-ray scattering

Small angle X-ray scattering is a very powerful technique to reveal the size, shape and internal structure of colloidal particles in solution. The investigated particles can be colloids, macromolecules like polymers or micelles with size ranges from 1 nm to 1 μm. In order to get information about the structure, shape and size distribution of such particles, the wavelength of the radiation, $\lambda$, used in the scattering experiment should match the size range of interest.\(^{[25,26,27]}\)

A highly collimated and monochromatic X-ray beam is focused on the sample, and the electron density variation between the particle and the matrix/solvent causes X-rays to scatter: this is the so-called electron density contrast $\Delta \rho(r) = \rho(r)-\rho_0$. The X-rays scattered reach the detector, and the two-dimensional scattering image is then integrated in a 1D scattering curve, $I(q)$, as a function of the scattering vector, $q$.\(^{[25,26,27]}\) Figure 4 illustrates the experimental setup of a synchrotron SAXS measurement.
Figure 4. Schematic representation of the small angle X-ray scattering experiment.\cite{28}

The scattering intensity $I(q)$ is equal to:

$$I(q) = N P(q) S(q)$$  \hspace{1cm} (3)

where $N$ is the number of particles per unit volume, $P(q)$ is called the form factor and is related to the scattering of a single isolated particle and $S(q)$ is called the structure factor and arises from interactions between particles.

In a dilute regime, interactions between particles do not occur and the total scattering is equal to the sum of the scattering intensities of the non-interacting particles. In this dilute regime, information about the shape, size and distribution of particles is gathered.

Since we are working in the reciprocal space, the object dimension is inversely proportional to $q$. The scattering at large $q$ values refers to small objects at small $q$-values to large structures.\cite{29} Thus, from equation 4, it is possible to calculate the dimension $d$ of an object:

$$q = \frac{2\pi}{d}$$  \hspace{1cm} (4)

For small-angle scattering, three regions can be distinguished as shown in Figure 5. The small $q$-range corresponds to the Guinier regime: the size of a particle, irrespective of whether it is geometrically well defined or irregular in shape, can be conveniently characterised by its radius of gyration $R_g$ according to the Guinier law. For spherical particles, the Guinier law is given by equation 5.\cite{29}
\[ I(q) = I(0) \exp \left( \frac{q^2 \langle R_g^2 \rangle}{3} \right) \] (5)

where \( I(0) \) is the scattering intensity at zero scattering angle. Therefore, the Guinier approximation is valid at \((q \ll 1/ R_g)\). The scattering intensity in the Porod regime writes:

\[ I(q) \sim q^{-s} \] (6)

where exponent \( s \) is equal to 4 for spheres (3D), 2 for thin disks (2D), and 1 for thin rods (1D), and is thus reflecting the dimensionality of the object.[30]

![Diagram](image)

**Figure 5.** Different scattering ranges and the corresponding structural information, which can be obtained by power laws.[29]

Using the applications and advantages of this technique, measurements of small angle X-ray scattering (SAXS) were carried out to determine the size, shape and polydispersity of the gold nanoparticles at SAXS1 beamline at the LNLS (Campinas, Brazil). The X-ray beam was at an energy of 8 keV (\( \lambda = 1.54 \) Å). The Pilatus detector placed at a distance of 1000 mm from the sample resulting in a \( q \)-range of 0.1 to 4 nm\(^{-1}\) (\( d \) ranging from 1.5 to 60 nm). We used the SASFIT software to model the collected data.
3. Results and discussion

3.1 Gold nanoparticles synthesised by chemical reduction with NaBH₄

The first evidence of formation of gold nanoparticles was by merely observing the colour of the solution, changing from yellow to red. This is due to the consumption of Au³⁺ ions and to the formation of AuNPs under the oxidation reduction reaction which occurs after addition of the reducing agent NaBH₄, according to the following reaction:

\[ 8\text{HAuCl}_4 \cdot 3\text{H}_2\text{O} + 3\text{NaBH}_4 \rightarrow 8\text{Au}^0 + 3\text{NaB(OH)}_4 + 12\text{H}_2\text{O} + 32\text{HCl} \]

The mechanism of reducing the gold occurs in two steps. First, the reduction of the yellow ions Au³⁺ to ions Au⁺ is occurring with a transparent coloration. This step is observed with the addition of the first aliquot of the reducing agent.

\[ \text{Au}^{3+} + 2e^- \rightarrow \text{Au}^+ \]

The second step is the reduction of Au⁺ to Au⁰, with the change of solution colour between violet and red.

\[ \text{Au}^+ + e^- \rightarrow \text{Au}^0 \]

This range of colorations between violet and red which the AuNPs samples can achieve depends on the efficiency of the stabilisation and size of the nanoparticles, therefore this stabilisation depends on the type of ionic liquid used and its concentration in solution.

Thus, the feasibility of using ionic liquids with different chain lengths, different anion and concentrations as stabilising agents of AuNPs is demonstrated.

3.1.1 Effect of chain length

As a first result, it was found that ionic liquids with the shorter chain length, C₂mimCl, C₄mimCl, C₆mimCl, C₄mimBr and C₆mimBr, did not form stable AuNPs. Shortly after the addition of the reducing agent (NaBH₄) blacks precipitates are formed in the reaction system, corresponding to large unstable reduced gold clusters. On the other hand, the samples synthesised in the presence
of ionic liquids of higher chain length, from C$_{10}$ to C$_{16}$, showed immediate formation of nanoparticles evidenced by coloration the solution ranging from violet to red. This difference of coloration is related to the size of the nanoparticles and can best be visualised by the moving SPR peak in the UV-Vis spectrum. Figure 6 shows the UV-Vis spectra of the synthesised AuNPs with ionic liquids of different chain lengths and same concentration of 100 mM.

![Figure 6](image_url)

**Figure 6.** UV-Vis spectra of AuNPs stabilised by 100 mM solution of ionic liquids with different chain length: (a) C$_{10}$mimCl (red), C$_{12}$mimCl (blue) and C$_{16}$mimCl (black); (b) C$_{10}$mimBr (black) and C$_{12}$mimBr (blue).

The UV-Vis spectra, for both ionic liquids with chloride and bromide anions, display a SPR peak shift indicating a variation in size of the NPs directly related to the length of the chain. Another important observation is the shape and width of the absorption peak variations indicating possible changes of shape and polydispersity of the samples. In the case of AuNPs stabilised by C$_{10}$mimCl (Figure 6a) the plasmon band has a higher absorption and a smaller width than the other two curves for nanoparticles stabilised by IL C$_{12}$ and C$_{16}$: their sizes are larger but their polydispersions are smaller. For a better visualisation of the effect of chain length on the size of the AuNPs, the diameter of the nanoparticles were estimated by the proposed Haiss and co-workers$^{[26]}$ method, and are presented in table 1. Note that the broadness of the SPR peak induces larger errors on the calculation of the sizes.
Table 1. Diameter of the gold nanoparticles calculated by UV-Vis and SAXS.

<table>
<thead>
<tr>
<th>Ionic liquid utilised</th>
<th>$\lambda_{spr}$ (nm)</th>
<th>$A_{spr}$</th>
<th>$A_{450}$</th>
<th>Diameter (nm) UV-Vis$^{(a)}$</th>
<th>Diameter (nm) UV-Vis$^{(b)}$</th>
<th>Diameter (nm) SAXS</th>
<th>Log-normal SAXS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{10}$ mimCl</td>
<td>514</td>
<td>3.22</td>
<td>2.82</td>
<td>2.57</td>
<td>3.40</td>
<td>5.42</td>
<td>0.43</td>
</tr>
<tr>
<td>C$_{12}$ mimCl</td>
<td>506</td>
<td>2.25</td>
<td>2.73</td>
<td>0.83</td>
<td>1.31</td>
<td>5.8</td>
<td>0.25</td>
</tr>
<tr>
<td>C$_{16}$ mimCl</td>
<td>500</td>
<td>2.60</td>
<td>2.28</td>
<td>2.55</td>
<td>3.39</td>
<td>3.16</td>
<td>0.205</td>
</tr>
<tr>
<td>C$_{10}$ mimBr</td>
<td>518</td>
<td>3.12</td>
<td>2.68</td>
<td>1.02</td>
<td>1.29</td>
<td>5.9</td>
<td>-</td>
</tr>
<tr>
<td>C$_{12}$ mimBr</td>
<td>500</td>
<td>2.66</td>
<td>2.83</td>
<td>1.25</td>
<td>1.85</td>
<td>4.22</td>
<td>0.49</td>
</tr>
</tbody>
</table>

(a) Diameter calculated by equation 2 (parameters $B1=3.55$; $B2=3.11$).
(b) Diameter calculated by equation 2 (parameters $B1=3.00$; $B2=2.20$).

First of all, we clearly observe that the nanoparticle size decreases with increasing chain length of the ionic liquid. Ionic liquids with short alkyl chain, i.e., with a smaller hydrophobic chain, have greater difficulty of self-organisation in aqueous medium and consequently are less protective towards the nanoparticle. There is no sufficient repulsion between the gold particles, thus causing the aggregates formation. Empirically, it is found that the natural logarithm of the critical micellar concentration (cmc) varies linearly with the number of carbon atoms in the hydrophobic chain, and the shorter the chain length, the greater the value of the cmc: this factor seems to directly influence the properties of the nanoparticles. On the other hand, the AuNPs synthesised through the protection of ionic liquids with long chain length have the smaller sizes. The greater hydrophobicity of the alkyl chain facilitates the self-organisation of ionic liquids in aqueous solution as well as providing an additional steric protection for the formation of nanoparticles. Thus, the possibility of aggregation is reduced with the increase of alkyl chain protection agent.

The nanoparticle size was also obtained by HR-TEM. The analysis of micrographs (Figure 7) allows us to confirm that the AuNPs obtained have spherical shape and sizes close to 5 nm.
Figure 7. HR-TEM images of AuNPs samples stabilised by 100mM: C$_{10}$mimCl (a), C$_{12}$mimCl (b), C$_{16}$mimCl (c), C$_{10}$mimBr (d) and C$_{12}$mimBr (e).

The size dependency of the AuNPs on the alkyl chain length of the ILs can be observed by on the SAXS curves shown in Figure 8. It is apparent that the samples display different $q$-dependencies. These dependencies relate not only about the size but also the shape of the objects. For the C$_{10}$mimBr one, the $q^{-1}$ behaviour at low $q$ values indicate the formation of linear objects, while for the C$_{12}$mimCl and C$_{16}$mimCl form small spherical nanoparticles. The diameters of AuNPs were calculated and are shown in Table 1.
Figure 8. SAXS curves of AuNPs stabilised by ionic liquids at 100 mM with different chain lengths: C_{10}mimCl (blue), C_{12}mimCl (green), C_{16}mimCl (pink), C_{10}mimBr (black) and C_{12}mimBr (red).

To check the stability of the synthesized nanoparticles, the UV-Visible spectroscopy measurements were repeated after a week and compared with baseline measurements. The UV-Vis spectra showing the changes of the profile curves are presented in Figure 9.

Figure 9. UV-Vis spectra of gold nanoparticles stabilised by ionic liquids with different chain length (a) C_{10}mimCl (red), C_{12}mimCl (black) and C_{16}mimCl (blue); (b) C_{10}mimBr (black) and C_{12}mimBr (blue). Where the solid lines correspond to samples measured on the same day of the synthesis and the dotted lines correspond to the sample measured after one week of synthesis.
From analysis of the Figure 9, we can see that all the samples show a shift in peak position corresponding to the surface plasmon resonance due to an increase in particle size as a function of time. However, it is apparent that this offset is more pronounced for samples stabilised by ionic liquids with shorter chain length than for higher ones. Additionally, it is seen that the peaks become better defined after one week, which may indicate that the particles become larger and with more uniform size distributions. Thus, we conclude that the stability of AuNPs increase with increasing hydrophobic chain length of the stabilising agent.

3.1.2 Effect of nature of anion

The comparison between the gold nanoparticles stabilised by ionic liquid chlorinated and brominated was done through analysis of UV-Visible spectroscopy, microscopy and SAXS.

The effect of the anion nature in the shape and size of AuNPs can be seen in micrographs (a) and (d) of Figure 7 relating to nanoparticles stabilised by ionic liquids C\textsubscript{10}mimCl and C\textsubscript{10}mimBr respectively. The AuNPs synthesised in the chlorinated IL are smaller, about 3 nm, and spherical while the ones in brominated IL are larger, 6-7 nm and have an ellipsoidal shape. Similarly, we observe the same effects of the anions on the AuNPs synthesised in C\textsubscript{12} chain length ILs (Figures 7 (b) and (e)).

Moreover, this effect is also observed by UV-Vis, in Figure 10, where the shift of the SPR peak, towards longer wavelengths for brominated compared to chlorinated ILs corresponding to an increase of the NPs size.
Figure 10. UV-Vis spectral changes of AuNPs stabilised by ionic liquid solution with concentration of 100mM of (a) C_{10}mimCl (black) and C_{10}mimBr (blue); (b) C_{12}mimCl (black) and C_{12}mimBr (blue)

The change in the nature of the counter ion by another one, that has greater polarsability or higher valence, causes greater interactions between the ion and the polar head of the IL molecule. This gives rise to the increase in the aggregation number and the decrease in the cmc.\[^{33}\] As a result, the difference on the profile of AuNPs obtained can be explained by the larger and polarsable anion Br\(^-\) which has weak hydration. Weaker hydrated anions are easily absorbed on the surface of the micelles and consequently decreases electrostatic repulsion\[^{34}\] and in this way facilitates the aggregation of the AuNPs. Comparing with the anion Cl\(^-\), these effects are minor, due to their smaller size and greater hydration.

3.1.3. Effect of concentration variation

Samples at concentrations of 10, 25, 50, 100 and 200 mM of ionic liquid were prepared to study the effect of concentration of ionic liquids on the stability and size of the gold nanoparticles. The UV-Vis spectra of the samples are shown in Figure 11.
**Figure 11.** (a) UV-Vis spectra of AuNPs in different concentrations of C\textsubscript{10}mimCl ionic liquids at 10 (yellow), 25 (blue), 50 (green), 100 (black) and 200 mM (red). (b) Diameters estimated by Equation 2 (using the parameters B1=3.0 and B2=2.2) of AuNPs samples stabilised by ionic liquids C\textsubscript{10}mimCl (black), C\textsubscript{12}mimCl (blue), C\textsubscript{16}mimCl (green) for concentrations from 10 mM to 200 mM.

Looking at the spectra of Figure 11a, it can be seen that a shift of the SPR peak of the relative concentration occurs, at smaller ionic liquid concentrations of 10 and 25 mM the SPR peak is located in the region of longer wavelengths due to the larger size the formed nanoparticles. At higher concentrations of ionic liquid can observe a shift of the SPR peak to shorter wavelengths.

Similar profiles curves of UV-Vis spectra were obtained for all samples AuNPs in ionic liquids at concentrations of 10 mM to 200 mM, but with some variations of tendency in relation at concentration. Thus, the Figure 11b shows the relationship between all chlorinated ionic liquids in all the concentrations and their respective estimated size by equation 2 (with parameters B1=3.0 and B2=2.2). We can be observe that with the increase of concentration the sizes of AuNPs decrease.

This concentration effect can be easily visualised by colour difference of samples AuNPs. The Figure 12 shows the change of colour of the samples prepared AuNPs with the C\textsubscript{10}mimCl ionic liquid, where one can see that the colour changes from violet to red due to increased concentration.
Figure 12. Photograph of samples of AuNPs stabilised by C\textsubscript{10}mimCl in the concentrations of 10 (a), 25 (b), 50 (c), 100 (d) and 200 mM (e).

This concentration effect can be explained by the mechanism proposed by Safavi and Zeinali\textsuperscript{[4]}. They stated that at low concentrations of ionic liquids, the latter interact with the halide ions adsorbed on the AuNPs surface and can neutralise the particles' charge. The particles begin to aggregate in water, and after several hours these aggregates precipitate from the solution. However, increasing the concentration results in a greater supply of IL’s cations which are able to attach to the nanoparticle’s surface by hydrophobic interactions between alkyl chains. Thus, the nanoparticles become stable and dispersed in the aqueous solution due to the electrostatic repulsion caused by the positively charged surface of the nanoparticles.

SAXS measurements of pure ionic liquid solutions (same concentrations as for the nanoparticles synthesis discussed above) were performed to better understand this concentration-dependent behaviour. The SAXS graphs for the solutions C\textsubscript{16}mimCl from 10 mM to 500 mM are shown in Figure 13a. We can observe the presence of three diffraction peaks, the first corresponding to the peak related to self-organised objects formed by the interaction of the ionic liquid with the aqueous medium. This is evident because we can observe its shift to higher q values with increasing concentration, which makes us understand that at very low concentrations as 10 mM, the ionic liquid chains are predominantly free, and therefore do not display diffraction. But with the gradual increase of the concentration, the chains begin to organise and form structures that will cause scattering. According to equation 4, the diameter of the object is inversely proportional to q (\(q=2\pi/d\)). The shift to higher q values is related to the formation of increasingly smaller and more compact objects due to the increased concentration of self-organised structures. This second peak is related to the size
of each molecule of imidazole cation participant to the self-organised structure of the object. Thus, using equation 4, we can estimate that these sizes range from 4.4 nm at a concentration of 500 mM to 6.95 nm at 25 mM.

The third peak is constant at all concentrations with a value \( q = 2.8 \text{ nm}^{-1} \) and is therefore related only to the length of the alkyl chain of the ionic liquid. We can confirm this by comparing the diameter calculated by the equation 4 with the theoretical value of the size obtained by the equation 6 proposed by Tanford, where \( n \) is the carbon number of the alkyl chain.\[^{[35]}\]

\[
l_c = 1.5 + 1.265n
\]

(6)

The result of alkyl chain size estimated by the equation 2 is 2.24 nm, whereas the value estimated by equation 6 is 2.174 nm. The results are consistent and therefore the third diffraction peak really belongs to the alkyl chain of ionic liquid.

**Figure 13.** (a) SAXS curves of C\(_{16}\)mimCl solutions at concentrations of 10 (black), 25 (red), 50 (blue), 100 (green) and 200 (pink) and 500 mM (yellow); (b) SAXS curves of AuNPs stabilised by ionic liquids C\(_{16}\)mimCl with different concentrations of 10 (black), 25 (red), 50 (blue), 100 (green) and 200 mM (pink). The black lines indicate the slopes of -4 and -1 in the regions of Porod and Guinier respectively, in the curves of SAXS.

Figure 13b displays the SAXS curves of AuNPs stabilised by C\(_{16}\)mimCl ionic liquid. The effect of the concentration on the stability and the size of the
nanoparticles is pointed out. At a concentration of 10 mM, as seen in the discussion of Figure 13a, there is not enough efficient protection of the AuNPs and they can aggregate with each others. Moreover, the linear behaviour at small angles indicates the presence of large aggregates. However, with increasing concentrations, the SAXS profiles evolve. For example, at 100 and 200 mM, self–organisation is occurring, protecting the AuNPs from aggregating. Thus, the nanoparticles are smaller and a displacement occur in the SAXS curves towards greater values of $q$. Additionally, the SAXS signal corresponding to the diffraction of the micelles of ionic liquid indicates a strong self-organisation.

The same interpretation of the SAXS curves can be made to the AuNPs stabilised by $C_{12}$mimCl, where we also can observe the effect of concentration on the nanoparticle’s size. For 10 mM of IL, there is a clear presence of linear aggregates, characterised by the strong $q^{-1}$ dependency at low $q$ values. Unlike for $C_{16}$mimCl, at higher concentrations, for $C_{12}$mimCl we do not observe the presence of the diffraction peak of self-organised ionic liquid, the AuNPs SAXS signal being much stronger.

**Figure 14.(a)** SAXS curves of AuNPs stabilised by ionic liquids $C_{12}$mimCl with different concentrations of 10 (black), 25 (red), 50 (blue), 100 (green) and 200 mM (pink). **(b)** Correlation between the radius estimated by SAXS (■) and the polydispersity (○) of AuNPs as a function of $C_{12}$mimCl as a function concentration.
The sizes of the nanoparticles stabilised by C\textsubscript{12}mimCl in concentrations of 10 to 200 mM were obtained by fitting the SAXS data with the form factor of a sphere and with a log-normal distribution on the radius. The radius and their corresponding polydispersity values are shown in Figure 14b. For the high IL concentrations, the AuNPs size is the smallest, $r < 1.5$ nm, but with a higher degree of polydispersity. On the other hand, for lower IL concentrations, the nanoparticles obtained are larger but with a lower degree of polydispersity and, nevertheless, they also form large aggregates.

Through the SAXS analysis, we clearly observe in the Porod region a $q^{-4}$ dependency, indicating spherical shaped nanoparticles. In the case of C\textsubscript{12}mimBr at low concentration, the 10 mM, we notice a second $q^{-4}$ behaviour at low q values: the spherical nanoparticles begin to form aggregates of spherical shape. This is shown in Figure 15, where the SAXS data were fitted with a bimodal distribution of spherical form factors leading to radius of the nanoparticles equals to 1.9 nm and polydispersity index of 0.37 and the radius of the aggregate formed of the nanoparticles equals to 8.4 nm with a lower polydispersity 0.18.

![SAXS curves](image)

**Figure 15.** SAXS curves of AuNPs stabilised by ionic liquids C\textsubscript{12}mimBr at 10 mM (■) and the model of bimodal spheres (red). The two $q^{-4}$ dependencies and the two Guinier regions are clearly displayed; the corresponding NPs and aggregates are illustrated.
Figure 16 shows the SEM micrographs that illustrate the different sizes of protected AuNPs, for several IL concentrations. The images (a - c) is visible again that the size decrease with the increase of concentration, for 100 mM the size decrease down to around 3 nm. AuNPs protected by \( \text{C}_{10}\text{mimBr} \) at 10 mM, show larger sizes and aggregates formation (Figure 16e). For higher concentration than 25 mM, we can see a reduced aggregation; individual nanoparticles are distinguishable (Figure 16f).

Figure 16. SEM micrographs of samples of AuNPs in \( \text{C}_{10}\text{mimCl} \) at 10 mM (a), 25 mM (b) and 100 mM (c); \( \text{C}_{12}\text{mimCl} \) 100 mM (d); \( \text{C}_{10}\text{mimBr} \) at 10 mM (e) and 25 mM (f).

The stability of gold nanoparticles was tested by UV-Vis spectroscopy measurements after one week of initial preparation. As a result, in many samples, a more or less pronounced shift in the SPR peak to longer wavelength values is seen especially for low IL concentration. We understand that there is an increase in nanoparticle size with time due to aggregation and this is mainly occurring for low concentration of the stabilising agent.
Particularly, the AuNPs samples synthesised with C\textsubscript{10}mimBr showed the most unstable behaviour in the concentration range 10 to 50 mM. Indeed, a precipitate was formed and the deposition of a gold mirror at the bottom of bottles occurred. This corresponds to the formation of metallic gold not nanoparticulated. The low concentration of ionic liquid, the bromide anion and the relatively small length of chain concomitantly contributed to this result.

Another important observation is that precipitation occurs at low IL concentrations for most samples, except for those with long chain length and the chloride anion: the latter do remain stable for a long period of time due the parameters already discussed.

### 3.2 Study of interaction between ionic liquids and Au\textsuperscript{3+}

During the study of samples Au\textsuperscript{3+} in ionic liquid, (without the addition of the reducing agent NaBH\textsubscript{4}), we observed that the IL of the serie 1-alkyl-3-methylimidazolium chloride has a considerable reduction character that is capable of reducing gold valence from 3+ to 1+. The reduction reaction involved occurs slowly and gradually and can easily be perceived by observing the gradual disappearance of the characteristic yellow colour of the solution of Au\textsuperscript{3+}.

The UV-Vis spectrum of Figure 17 illustrates the reduction by C\textsubscript{12}mimCl 100 mM of the solution of Au\textsuperscript{3+}, one week after sample preparation by the decrease of the absorbance in the 322 nm region characteristic of Au\textsuperscript{3+}.  

![UV-Vis spectrum](image)

**Figure 17.** UV-Vis spectrum of the sample Au\textsuperscript{3+} in solution of the IL C\textsubscript{12}mimCl at 100 mM on the day of preparation (black) and one week later (blue).
The reduction of the gold is slower or faster depending on the chain length of the ionic liquid and its concentration, so that it was observed that the samples C_{16}mimCl showed a more pronounced and more rapid reduction compared to C_{12}mimCl and C_{10}mimCl. The spectrum of Figure 18 compares the effect of reduction in three different ionic liquids with chain lengths of C_{10}, C_{12} and C_{16}.

**Figure 18.** UV-Vis spectrum of the sample Au^{3+} in solution of the ionic liquid C_{10}mimCl (blue), C_{12}mimCl (red) and C_{16}mimCl (green).

Visualising Figure 18 it can be seen that the sample C_{16}mimCl has the lowest absorbance at 322 nm, thus showing its greatest reducing power compared to ionic liquids with shorter chains. Samples with ionic liquids C_{10}mimCl and C_{12}mimCl present similar profiles, possibly due to little difference in chain lengths. The concentration of ionic liquid also strongly influences the reduction rate, the higher the concentrations of IL, the more significant and the quicker the reduction of gold occurs. The spectrum of Figure 19 shows this effect, and demonstrates the reduction in absorbance in the region Au^{3+} of 322 nm due to the increase of the concentration of C_{16}mimCl. In the concentration of 500 mM, gold is totally reduced to Au^{1+} a few hours after mixture.
The brominated ionic liquids do not have the same reducing power as the chlorine one, due to the formation of a stable orange complex. The Figure 20 presents the UV-Vis spectra of the measures on the day of sample preparation and after one week of a solution of Au$^{3+}$ in C$_{10}$mimBr at 100 mM.

**Figure 19.** UV-Vis spectrum of the sample Au$^{3+}$ in solution of the ionic liquid C$_{16}$mimCl in the concentrations of 50 (blue), 100 (red), 200 (green) and 500 mM (black).

**Figure 20.** UV-Vis spectrum of the sample Au$^{3+}$ in solution of the ionic liquid C$_{10}$mimBr in a concentration of 100 mM on the day of preparation (black) and one week later (blue).
3.3 Samples reduced by X-ray irradiation

From the confirmation of reducing characteristics of ionic liquids, the solutions of Au\(^{3+}\) in a solution of 1-alkyl-3-methylimidazolium chloride (and bromide) were irradiated with X-rays. Ma and co-workers\[^{36}\] proposed a mechanism of formation of gold nanoparticles from X-ray irradiated ionic liquid. They explain that when an ionic liquid is irradiated, a strong reducing electron solvated (\(e_{\text{sol}}^{-}\)) is formed instantly. Under protection and reduction of an ionic liquid, the Au cation, surrounded by chloride ligands, is gradually reduced due the action of \(e_{\text{sol}}^{-}\). Au-Au bonds begin to form when the coordination number of the Au-Cl bond is reduced to two. Thereafter, more Au ions begin to gather into clusters, and AuNPs clad with Cl are finally produced.\[^{36}\]

\[
\text{Au}^3+ + 3\text{Cl}^- \rightarrow \text{Au}^2+ + 3\text{Cl}^- \\
\text{Au}^2+ + \text{Cl}^- \rightarrow \text{Au}^{\delta-2} + \text{Cl}^- \\
\text{Au}^{\delta-2} + \text{Cl}^- \rightarrow \text{Au}^{\delta-4} + \text{Cl}^- \\
\text{Au}^{\delta-4} + \text{Cl}^- \rightarrow \text{Au}^{\delta-2} + \text{Cl}^- \\
\text{Au}^{\delta-2} + \text{Cl}^- \rightarrow \text{Au}^{\delta-4} + \text{Cl}^-
\]

**Figure 21.** A schematic of the formation mechanism of gold nanoparticles by X-ray irradiated ionic liquid.\[^{36}\]

This mechanism can be generalised to the ionic liquid with chloride and bromide, but the difference in the results obtained by both synthesis is explained by differences between the anions already mentioned in section 3.2. For the synthesis of gold nanoparticles using the ionic liquids with bromide 10 times longer exposure times were necessary compared to the samples with chloride IL. Therefore, it becomes apparent the lower efficiency of bromide IL to reduce the gold.

The in situ synthesis of gold nanoparticles by X-ray irradiation is shown in Figure 22a where the scattering intensity \(I(0)\) is increasing with time and thus X-ray dose. This increase of \(I(0)\) is related to the formation of AuNPs by reduction of Au\(^{3+}\) in a solution of ionic liquid C\(_{12}\)mimCl at 50 mM.
Figure 22. (a) Relation between the scattering intensity and exposure time/X-ray dose for AuNPs (C\textsubscript{12}mimCl, 50 mM). (b) SAXS 3D graph of the variables time, scattering vector and intensity of \emph{in situ} synthesis of gold nanoparticles by X-ray irradiation and with the stabilisation by C\textsubscript{12}mimCl.

To better illustrate the kinetics of formation of AuNPs, we present in Figure 21b the 3D-SAXS graph of the formation of AuNPs by X-ray irradiation. We clearly observe the formation and growth of the AuNPs with time, the SAXS intensities increasing and their profiles displaying clear Guinier and Porod (-4) regimes. Moreover the evolving SAXS profiles towards smaller \(q\) values indicates the growth of AuNPs.

The size of the spherical AuNPs as a function of time, were calculated from equation 5 and the results are shown in Figure 23, in which we can see the exponential increase in nanoparticle size with increasing time of exposure to X-ray irradiation. The nanoparticles grow with time to reach a radius of 1.8 nm after 3 minutes irradiation and a polydispersity of 0.3. It is clear that the distribution of sizes decreases with growing NPs size.
Figure 23. Evolution of the sphere radius and polydispersity of AuNPs synthesised by X-ray irradiation as a function of time.

Through all the obtained kinetic data, we can see the possibility of obtaining the desired AuNPs sizes controlling the exposure time of the X-ray irradiation, which is presented as one of the biggest advantages of this method of reducing.

4. Conclusions

In this work, gold nanoparticles stabilised by ionic liquids of Imidazolium family were synthesised and characterised by multiple complementary techniques, with the objective of understanding the effect of the variation of several factors related to the structure and concentration of IL in the formation, stability, size and shape of gold nanoparticles.

From the results obtained by UV-Vis spectroscopy, HR-TEM, SEM and SAXS we draw the following conclusions:

- The sizes decrease with the increase of chain length of the ionic liquid.
- The sizes decrease and the stability increase with the increase of concentration of ionic liquid.
• Gold nanoparticles are smaller and more stable for ionic liquids with chloride anion than with the bromide anion.
• At higher concentrations of all ionic liquids, spherical nanoparticles are obtained, and at low concentrations aggregate formation occurs.
• By X-ray irradiation it is possible to quickly obtain small and spherical nanoparticles, with the possibility to control size as a function of exposure time.

Therefore, through this study, it was possible to elucidate the most important effects that occur in the characteristics of gold nanoparticles due to variations of the protective agent. However it was not fully understood how the action of bromine and chlorine anions in the protection of the gold nanoparticles occurs. Thus, as a continuation of this work, getting a better insight into the coordination properties of gold in room temperature ionic liquids before the reduction in gold metal could enable to shed light on the anions functions. The EXAFS technique could be used, as it can provide information about the structural and electronic environment of gold when dissolved in ionic liquids and before and after the chemical reduction. EXAFS experiments carried out at the Au L_{III} edge and Br K edges would certainly contribute also to understand the effect of synthesis conditions on the formation specific sized/ shape gold nanoparticles, as well as the effects on their monodispersity and stability.
5. References


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