Chapter 5

Synthesis of Stabilized Transition Metal Nanoparticles Using Ionic Liquids
Metal particles smaller than 100 nanometers in primary particle diameter are generally considered as NPs (nanoparticles). Such M-NPs (metal nanoparticles) often exhibit very interesting electronic, magnetic, optical, and chemical properties. As an example, their high surface-to-volume ratios have large fractions of metal atoms at surface available for catalysis.\textsuperscript{1-3}

In Section 1.9 the effect of ILs (ionic liquids) in the stabilization and formation of nanoparticulate systems has been discussed. In this section, the synthesis of transition M-NPs viz. cobalt, copper and silver is being reported. Various ILs have been used for the stabilization of these nanomaterials. Most of these RTILs (room temperature ionic liquids) were found to provide a protective layer (via electrosteric stabilization) so as to prevent oxidative degradation and agglomeration of the particles. The study also focuses on effect of certain structurally different ILs on the size and morphology of these M-NPs. Chemical reduction method, using the corresponding metal salt and an appropriate reducing agent in a polar solvent and IL as a stabilizer, was employed for the synthesis of the respective M-NPs. This chapter has been thus divided into three sections incorporating the synthesis of various transition M-NPs. Various parameters such as effects of solvent, concentration of metal ions, reducing agent and effect of IL has been carefully looked into so as to see their effect on the particle synthesis. Finally, the synthesized particles have been characterized using UV-Vis, DLS, TEM, E-DAX, SEM, XRD and ZETA potential analysis.
SECTION 5A

Synthesis of magnetic cobalt nanoparticles using chemical reduction method

In this section, a quick and efficient process for the synthesis of magnetic cobalt nanoparticles in a polar aprotic media and stabilized using different ILs is being presented. ILs with their unique cation and anion structure were presumed to form a characteristic network around the particle periphery without affecting their catalytic active sites. Various parameters were tuned during initial studies including screening for an appropriate solvent, reducing agent, concentration of reducing agent and the method to be adopted for the reduction reaction. Formation of cobalt nanoparticles was thereby confirmed and results analyzed by Dynamic light scattering (DLS) studies, XRD, TEM, SAED, EDAX, SEM and UV-Visible studies.

\[ \text{CoCl}_2 + 2\text{NaBH}_4 \rightarrow \text{Co} + 2\text{NaCl} + \text{B}_2\text{H}_6 + \text{H}_2 \uparrow \]

Scheme 5A.1: Reduction of CoCl\(_2\) with NaBH\(_4\)

Figure 5A.1: Color transitions from CoCl\(_2\) to Co NPs
5A.1 INTRODUCTION

Nano-sized particles (NPs) made up of a few to some thousand atoms have attracted a widespread interest for their peculiar physical properties. These special properties are mainly due to their finite size and huge surface to volume ratio, which implies the presence of a large number of surface atoms having coordination different from that of bulk atoms. Moreover, the small size of the NPs, comparable with (or even smaller than) the coherence lengths of the electrons, modifies their electronic properties and their response to external fields. In particular metallic NPs may show an ample variety of phenomena such as super-paramagnetism, magneto-resistance, magnetic anisotropy etc.,\(^4\) which can be relevant for innovative applications in very different fields ranging from medicine to microelectronics, magnetic storage devices and sensors.\(^5\)

**Transition metallic** (Fe, Co, Ni) nanoparticles have found wide application in catalysis, solar energy absorption and magnetic recording.\(^6,7\) Magnetic nanoparticles are also a very promising tool for several **biomedical applications**. Heat generation of these particles in a magnetic AC field can be used for local hyperthermia in the therapy of tumors.\(^8,9\)

According to studies by Dobson *et al* research is being conducted into magnetic twisting cytometry, a process in which ferromagnetic microspheres are bound to specific receptors on a cell wall. Changing the direction of an applied magnetic field twists the microsphere by a measurable amount, which can then be related to the mechanical properties of the cell membrane and cytoskeleton.\(^10-14\) Magnetic nanoparticles are also being tested for tissue engineering applications (for example, in the mechanical conditioning of cells growing in culture).\(^15-17\) In such systems, magnetic particles are attached to either the cell membrane, or to mechano-sensitive ion channels in the membrane and a magnetic force is applied which activates the channels and initiates biochemical reactions within the cell, thereby promoting the growth of functional bone and cartilage. A third example
has been cited for magnetic biosensing: using magnetic nanoparticles coupled to analyte specific molecules to detect target molecules.\textsuperscript{18,19}

Of the three transition metals (Fe, Co, Ni) that are normally ferromagnetic, the nanoparticles of pure cobalt probably have special significance in both theory and technology,\textsuperscript{20-22} because there exists uniaxial hexagonal close-packed (HCP or $\alpha$-cobalt) structure besides face-centered cubic (FCC or $\beta$-cobalt) structure.\textsuperscript{23} Cobalt-based nanoparticles reside as the most promising materials for technological applications like information storage, magnetic fluids and catalysts.\textsuperscript{24,25} These have also been demonstrated to have potential for heating applications.\textsuperscript{26} Thus, in most of the cases cobalt (Co) nanoparticles, they are expected to possess exceptionally high-density magnetic property, sintering reactivity, hardness levels, excellent impact resistance properties, etc.

Many studies on synthesis and magnetic properties of other M-NPs such as Fe, Au, Pd, and composites have been reported.\textsuperscript{27-30} However quite a few have been reported for the preparation of cobalt nanoparticles.\textsuperscript{21,22,31-35} Cobalt nanoparticles have also been prepared by reduction of cobalt salt in hydrazine alkaline system\textsuperscript{35} and this involves the application of ultrasound initiative.\textsuperscript{23}

ILs have been evidenced with promising applications for synthesis, extraction and stabilization of M-NPs and other inorganic nanostructures.\textsuperscript{36} As far as applications of ILs for the preparation and stabilization of cobalt nanostructures is concerned, it has been observed that the Co nanowires electrodeposited from mixture of 1-ethyl,3-methylimidazoliumchloride ([emim]Cl) ionic liquid and ethylene glycol have a smoother surface and better magnetic properties than Co nanowires electrodeposited from aqueous solution. Moreover, they show a better squareness, so that the cobalt nanowires electrodeposited from mixture of [emim]Cl ionic liquid and ethylene glycol using PAA template can be applied to a perpendicular magnetic recording film.\textsuperscript{37}
In our experimental studies we have tried synthesis of cobalt nanoparticles using a method of sonication. Sonochemistry has often been applied for the synthesis of nano sized materials.\textsuperscript{38-43} The ultrasound irradiation of a liquid results in cavitation (the implosive collapse of bubbles) that creates localized “hot spots” with effective temperatures of 5000 K, high pressure and lifetimes of the order of a few nanoseconds or less.\textsuperscript{44} The effect of ultrasonic irradiation on chemical reactions is to accelerate them and to initiate new reactions that are difficult to carry out under normal conditions.\textsuperscript{45} In the past, the extreme conditions attained during the collapse of bubbles have been exploited to prepare amorphous metals, alloys, carbides, oxides, hydroxides, sulfides and composite nanoparticles.\textsuperscript{40,46-58}

In this section we have observed the effect of various ILs on the size of cobalt nanoparticles so formed from sonochemical synthesis involving reduction of CoCl\textsubscript{2}.6H\textsubscript{2}O with NaBH\textsubscript{4} as carried out in polar aprotic medium of dimethylsulfoxide. The method gives an advantage over most of the previous other methods cited in the literature like low yields in reverse miceller method, high temperature requirements and toxic effects of stabilizers such as chemical surfactants.

5A.2 RESULTS AND DISCUSSION
CoCl\textsubscript{2}.6H\textsubscript{2}O was used as a precursor to synthesize cobalt nanoparticles in the chemical reduction method using sodium borohydride as the reducing agent and an IL as a stabilizing agent in a polar aprotic solvent media. As in each method of nanoparticle synthesis involving chemical reduction, the reducing agent plays a crucial role in determining the chemical composition of the product so formed, in this case the choice of reducing agent was established by reacting an aqueous solution of 0.01M CoCl\textsubscript{2}.6H\textsubscript{2}O with 0.01M hydrazine hydrate. It was observed that a pink precipitate of cobalt- hydrazine hydrate complex was formed. However, this complex could be further treated with an alkali to yield cobalt NPs. But this was avoided so as to prevent a second step which followed an exothermic course.
When 0.01M of CoCl$_2$.6H$_2$O was reacted with an aqueous solution of sodium borohydride, a black precipitate was obtained but the yield of the precipitated cobalt was low due to the reactivity of sodium borohydride with water leading to the evolution of hydrogen. In order to optimize the right procedure for the synthesis of cobalt NPs, a number of parameters were varied and these included varying the solvent polarity, reducing agent concentration and the order of addition of ionic liquid in the chemical reduction process.

5A.2.1 Optimization of solvent for the synthesis of cobalt nanoparticles

In this experiment 0.01 M CoCl$_2$.6H$_2$O solution in an appropriate solvent (Table 5A.1) was reacted with a solution of sodium borohydride solution in the same solvent.

A series of solvents have been studied, starting with ethylene glycol. It was observed that when ethylene glycol was taken as solvent to react 0.01M CoCl$_2$.6H$_2$O with sodium borohydride, the reduction was incomplete even when the concentration of the latter was increased to 100 times, as indicated by the retained pink color of the cobalt ions in the solution (Figure 5A.1 (a)). It may be presumed that the chemical interaction between ethylene glycol and sodium borohydride prevented the reduction of cobalt (II) ions to cobalt in zero valent state. DLS measurement (for determining the size of the particles so formed dispersed in ethylene glycol solution) also indicated incomplete reduction and a mean particle size of around 290nm was obtained (Figure 5A.1(b)). Determining the area under each peak showed that only 59% of the particles in the colloidal solution fell in the nanometer range (Figure 5A.1(c)) and hence stabilization using a suitable ligand in the form of surfactant or IL was desirable.
Figure 5A.1: Reduction of CoCl$_2$.6H$_2$O in ethylene glycol; (a) Pink color of solution due to Co(II) ions is retained even after increasing reducing agent concentration indicating incomplete reduction (b) DLS data of isolated cobalt nanoparticles dispersed in ethylene glycol (c) Area under the peak tabulation of the DLS plot

When water was taken as a solvent for carrying out the reduction of 0.01M Co (II) ions using sodium borohydride, hydrogen gas evolved indicative of the borohydride ions reacting with water. Concentration of reducing agent available for reduction was therefore too low. Moreover, the product obtained agglomerated at the bottom indicative of the absence of a stabilizing agent and thereby negating water as the solvent of choice. Immediate DLS measurement of the solution obtained following sonication showed 71% of colloidal particles in solution with an average size of 48nm (Figure 5A.2 (a-c)). TEM images of the particles isolated from the reaction mixture immediately after the reaction also presented an agglomerated mass (Figure 5A.2 (d)). However, after 24hrs the black agglomerated precipitate turned green (Figure 5A.2 (e)) indicative of degradation of the particle due to oxidation.
Figure 5A.2: Reduction of CoCl$_2$.6H$_2$O in water; (a) Cobalt precipitates as black agglomerates in water. (b) DLS measurement plot of the solution upon sonication (c) Area under the peak tabulation of the DLS plot (d) TEM images obtained immediately after reaction (e) Cobalt agglomerates turn green in the absence of a stabilizing agent nearly after 24 hours

In the presence of a polar protic solvent methanol (commonly used for the synthesis of M-NPs in chemical reduction method) the precipitated cobalt agglomerates turned yellow (Figure 5A.3) and these were unsuitable for DLS measurement.
Polar aprotic solvents tetrahydrofuran (THF) and 1,4-dioxane were also investigated in this context. Both the solvents gave blue colored solutions on dissolving CoCl$_2.6$H$_2$O. However, sodium borohydride was completely insoluble in THF and so an aqueous solution of the latter was added for the reduction, which resulted in the formation of an infusible solid black mass (Figure 5A.4 (a)). This was separated and dispersed in a suitable solvent i.e. ethylene glycol using ultra-sonication and the size was measured using DLS/QELS (Figure 5A.4 (b)).

**Figure 5A.4:** (a) Reduction of CoCl$_2.6$H$_2$O in THF using aqueous sodium borohydride: Cobalt precipitates as infusible mass. (b) DLS measurement plot of the solution upon sonication. (c) Area under the peak tabulation of the DLS plot.
When 1,4-dioxane: water (8:2) solution of cobalt chloride was treated with sodium borohydride in the same solvent, a black mass precipitated out (Figure 5A.5 (a)) which was not at all dispersible in the solvent system. The agglomerated mass was separately dispersed into another solvent (ethylene glycol) and the size of the colloidal particles was measured using DLS (Figure 5A.5 (b)). Less than 65% of the particle were found to be in the size range of 30 nm-31 nm.

DMSO as a solvent for the reduction of CoCl$_2$·6H$_2$O with sodium borohydride gave an optically clear intense black solution (Figure 5A.6 (a)) from an initially blue colored solution. Absence of coalescence (leading to agglomeration in the initial phase) in this case was one of the reasons for choosing DMSO as the solvent of choice. Moreover, sodium borohydride could be dissolved and it did not react with the solvent system unlike in the water, methanol and ethylene glycol systems. DLS measurement of the reaction mixture afforded an average particle size of 20 nm with a polydispersity index of 0.581 (Figure 5A.6 (b)). It was observed that after 7-8 hours agglomeration was visible leading to increased particle size and this emphasized the need of a stabilizing agent.
Encouraged by the successful solvation properties of DMSO, previously tried solvents were used in conjunction with DMSO so as to see the effect of changing polarities. It is to be noted that only those solvents were adopted for this study which did not react with sodium borohydride. First in the series was DMSO-THF (1:1) which gave a black precipitate, while DMSO-1,4-dioxane (1:1) gave a fibrous black precipitate. A comparative view before and immediately after the reaction is given in Figure 5A.7 (a-b) and Figure 5A.8 (a-b) and the DLS data is also shown. DMSO-THF solvent mixture gave a distribution of cobalt nanoparticles as illustrated by the DLS data (Figure 5A.7 (b)) while the DMSO-1,4-dioxane mixture gave better results (Figure 5A.8 (b)). Thus, the performance of these polar aprotic solvents THF and 1,4-dioxane tremendously improved when taken in conjugation with DMSO. But using these mixtures for particle synthesis was limited by the deterioration in the stabilities of the particles with progression in time.
Figure 5A.7: (a) CoCl$_2$H$_2$O in DMSO-THF solvent system (b) Reduction of CoCl$_2$H$_2$O using sodium borohydride in DMSO-THF (c) DLS measurement plot of the solution upon sonication (d) Area under the peak tabulation of the DLS plot

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<th>Position</th>
<th>STD</th>
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<td>55.48</td>
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<td>1.1e+4</td>
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Figure 5A.8: (a) CoCl$_2$H$_2$O in DMSO-1,4-dioxane solvent system (b) Reduction of CoCl$_2$H$_2$O using sodium borohydride in DMSO-1,4-dioxane (c) DLS measurement plot of the solution upon sonication (d) Area under the peak tabulation of the DLS plot

<table>
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<td>2.6e+5</td>
<td>1.3e+5</td>
<td>2.1e+5</td>
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Based on the data for all the solvents and solvent systems discussed above (and as tabulated in Table 5A.1) for the reduction of CoCl$_2$6H$_2$O, DMSO was selected as the solvent of choice for further studies owing to its unique property in dispersing the metal nanoparticles so formed.

Table 5A.1: Solvent optimization for synthesis of cobalt nanoparticles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Observation</th>
<th>Particle size (nm), percentage of particles in that size range</th>
<th>Inference</th>
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<tr>
<td>5A.1.1</td>
<td>Ethylene glycol</td>
<td>Little Black precipitate</td>
<td>215 (60%)</td>
<td>Incomplete reduction</td>
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<tr>
<td>5A.1.2</td>
<td>Water</td>
<td>Black precipitate turned Green</td>
<td>48 (72%)</td>
<td>Cobalt oxide precipitate</td>
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<td>5A.1.3</td>
<td>Methanol</td>
<td>Black to yellow precipitate</td>
<td>Not in colloidal range</td>
<td>Degradation due to oxidation</td>
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<td>5A.1.4</td>
<td>THF</td>
<td>Black infusible precipitate</td>
<td>31 (81%)</td>
<td>Solid liquid phase separation</td>
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<tr>
<td>5A.1.5</td>
<td>1,4-dioxane</td>
<td>Black infusible precipitate</td>
<td>31 (64%)</td>
<td>Solid liquid phase separation</td>
</tr>
<tr>
<td>5A.1.6</td>
<td>DMSO</td>
<td>Black colloidal solution. No agglomeration till 7-8 hours</td>
<td>20 (90%)</td>
<td>Complete reduction. Stabilizing agent required</td>
</tr>
<tr>
<td>5A.1.7</td>
<td>DMSO-THF</td>
<td>Black colloidal solution, agglomeration in 30 min</td>
<td>49 (72%)</td>
<td>Rapid agglomeration due to THF</td>
</tr>
<tr>
<td>5A.1.8</td>
<td>DMSO-1,4-dioxane</td>
<td>Black colloidal solution, agglomeration in 20 min</td>
<td>28 (88%)</td>
<td>Rapid agglomeration due to 1,4-dioxane</td>
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5A.2.2 Optimizing the reducing agent concentration

The concentration of the reducing agent (RA) is an important factor for obtaining a complete reduction and has an influence on the size and stability of the particles formed at each stage. In order to conduct the reduction of 0.01M CoCl$_2$6H$_2$O, the concentration of sodium borohydride was varied from a minimum of 0.01M to a maximum of 0.05M (Figure 5A.9). It was observed that at equimolar concentration of the metal ion and the reducing agent, the reduction was incomplete as indicated by the
color of the reaction mixture (slightly greenish) and as in conjunction with the stoichiometry of the reaction (Scheme 5A.1). However, as the concentration of the RA was increased progressively, the color of the solution changed. DLS data for the individual reaction mixtures have been plotted in Figure 5A.10 (a-e). It was observed that as the RA concentration was increased, the percentage of particles under 30nm range increased. This observation could be supported by the earlier observations where cobalt nanoparticles obtained using varied solvent systems were obtained only in the range of 20nm-150nm and not beyond that. However, agglomeration was observed after some time indicating the need for stabilization.

UV-Visible absorbance study was also conducted to ensure the completion of reduction as indicated by a shift in $\lambda_{\text{max}}$ value from an initial value of 680nm (for CoCl$_2\cdot$6H$_2$O) to lower values with increasing concentration of sodium borohydride (Figure 5A.11). As the sodium borohydride solution was added to a solution of 0.001M solution of CoCl$_2\cdot$6H$_2$O in DMSO, a hypsochromic shift was observed. Peak for Co$^{2+}$ ions observed at 680nm started disappearing, while a new peak appeared around 450nm, indicating the formation of cobalt nanoparticles in the solution. Thus, it could be deduced from the absorbance studies that for the reduction of 0.001M solution of Co$^{2+}$ ions the optimum reducing agent concentration should be around 0.0056M (approximately five times the concentration of metal ions).

![Figure 5A.9: Reduction of 0.01M CoCl$_2\cdot$6H$_2$O in DMSO using (a) 0.01M (b) 0.02 M (c) 0.03 M (d) 0.04 M (e) 0.05 M sodium borohydride solution prepared in DMSO.](image-url)
Figure 5A.10: DLS data for the reduction of 0.01M CoCl₂·6H₂O in DMSO using (a) 0.01M (b) 0.02 M (c) 0.03 M (d) 0.04 M (e) 0.05 M sodium borohydride solution prepared in DMSO.
Figure 5A.11: UV-Visible absorbance spectrum study for the formation of cobalt nanoparticles using CoCl$_2$.6H$_2$O. Spectrum 1 indicates that of 2ml of pure 0.001M CoCl$_2$.6H$_2$O solution. Subsequent spectrum lines are for 50µl addition of addition of 0.05M sodium borohydride solution.

5A.2.3 Influence of ionic liquids (ILs) on size of cobalt nanoparticles

It has been found that ILs play a crucial role in the stabilization and formation of metal nanoparticles. In this study, certain room temperature ionic liquids (RTILs) and other molten salts with melting temperature under 100°C were considered. The standard chosen in this case was cobalt NPs dispersed in DMSO (prepared using 0.01M CoCl$_2$.6H$_2$O and 0.05M sodium borohydride solution). DLS measurements for this standard gave particles with a mean size of 27nm and polydispersity index of 0.517 (Figure 5A.12(a)). This reaction was carried out in eight individual sets and to each of these sets, immediately after the addition of the reducing agent, 100µl of an IL or its saturated solution in DMSO was added (Table 5A.2). DLS data as compiled in Figure 5A.12 (a-h) illustrates the effect of various ILs under study over the size and polydispersity of the cobalt nanoparticles so formed in the chemical reduction process.
In case of imidazolium ILs [bmim]BF₄ (Entry 5A.2.3, Table 5A.2, Figure 5A.12 (c)) and morpholinium ILs like [bmmor]BF₄, (Entry 5A.2.7, Table 5A.2, Figure 5A.12 (g)) it was observed that the more asymmetric and bulky imidazolium cation served better towards steric clouding and formed particles with peripheral boundaries, whereas relatively smaller morpholinium cation with a concentrated charge at a single nuclei was comparatively less effective towards steric clouding. The smallest tetramethylammonium cation [Me₄N]Br destabilised the particles so formed (Entry 5A.2.5, Table 5A.2, Figure 5A.12 (e)). Thus, it could be said that a bulkier cation provided the necessary geometry for steric repulsion such that the approach of two NPs colliding together to form an agglomerated mass could be rendered ineffective.

It could be observed that functionalized imidazolium ionic liquid, [C₁COOHmim]Cl, bearing carboxyl group at the terminus of imidazolium alkyl pendant chain, led to the degradation of the particles so formed as indicated by the DLS measurement (Entry 5A.2.2, Table 5A.2, Figure 5A.12 (b)). However allyl functionalized morpholinium ionic liquid [ammor]Br (Entry 5A.2.4, Table 5A.2, Figure 5A.12 (d)) led to prolonged stabilization for many days. Thus, presence of a functional group also enhanced the stabilization in certain cases (depending on the nature of the functional group).

In addition it was observed that it was not only the cation but also the anion which helped in stabilization. Non-functionalized imidazolium chloride ionic liquid, [bmim]Cl led to an increase in polydispersity and size (Entry 5A.2.6, Table 5A.2, Figure 5A.12 (f)), whereas [bmim]BF₄ led to a decrease and enhanced stabilisation. Thus, it is not only the cation but also the anion which affects the particle growth. Here in the case of an anion there exists a charged or electrostatic interaction between the surface of the nanoparticle and the layer of anionic charge (as according to DLVO theory) (Section 1.9.2).
Figure 5A.12: DLS data cobalt nanoparticles stabilized with different ionic liquids (a) no ionic liquid (b) [C$_1$COOHmim]Cl$^{[59]}$ (c) [bmim]BF$_4^{[60]}$ (d) [ammor]Br$^{[61,62]}$ (e) Tetramethylammonium bromide (f) [bmim]Cl$^{[63]}$ (g) [bmmor]BF$_4^{[63]}$ (h) [Hmmor]NO$_3^{[64]}$.

$^a$Reaction conditions: 0.01M CoCl$_2$6H$_2$O reduced using 0.05M Sodium borohydride solution in DMSO as solvent.
Table 5A.2: Influence of ILs over size and polydispersity of cobalt nanoparticles\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry No</th>
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<th>Ionic liquid (Name)</th>
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<th>Polydispersity</th>
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<td>-</td>
<td>27</td>
<td>0.517</td>
</tr>
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<td>0.796</td>
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<tr>
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<td>0.976</td>
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<td>1.963</td>
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<td>[Hmmor]NO\textsubscript{3}</td>
<td>40</td>
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\textsuperscript{a}Reaction conditions: 0.01M CoCl\textsubscript{2}.6H\textsubscript{2}O reduced using 0.05M Sodium borohydride solution in DMSO as solvent.

Thus, amongst the various ILs chosen for study, bulky imidazolium cation with a small counter anion (such as bromide or tetrafluoroborate) could provide steric as well as electrostatic stabilization, collectively known as electro-steric stabilization effect.
Moreover, the high viscosity of ILs could be an additional factor minimizing the probability of close contacts between the particles leading to large particle size.

5A.2.4 Transmission Electron Microscopic analysis (TEM) of cobalt nanoparticles

Transmission electron microscopic studies were carried out for the cobalt NPs prepared with and without using an ionic liquid. Based on the studies in Section 5A.2.3, cobalt NPs synthesized using the ionic liquid [bmim]BF₄ were the core of the study. In order to prepare the samples for TEM analysis 5mg of the dry NPs were dispersed in 25ml of ethanol using an ultrasonicator and this yielded a clear dispersed solution of NPs. 10µl of this solution was dropped over a carbon coated copper grid and grid was dried in a vacuum desiccator for a few hours. The dried grid was then examined under an electron microscope (TEM TECHNAI 300KV, Ultra twin FEI with EDAX transmission electron microscope operating at 300 kV). Figure 5A.13 (a-c) presents the TEM images of cobalt NPs prepared using standard chemical reduction method (using 0.01M CoCl₂.6H₂O and 0.05 M sodium borohydride solution at room temperature). Figure 5A.14 (a-d) represents cobalt NPs isolated from the solution where the former had been stabilized using the room temperature ionic liquid [bmim]BF₄. Comparison revealed that cobalt NPs prepared without capping with a suitable ligand (as in this case an ionic liquid) did form an agglomerated mass, whereas those capped by ILs were dispersible as shown in Figure 5A.14 (b). Clearly NPs stabilized using an ionic liquid appeared differently in the TEM micrographs indicating the need of a stabilizing agent to prevent rapid coalescence amongst the formed particles. The stabilized particles formed were uniform and spherical in shape, with a size range of about 20-25nm.
Figure 5A.13 (a-c) TEM images of bare cobalt nanoparticles
*Reaction conditions: 0.01M CoCl₂.6H₂O reduced using 0.05M Sodium borohydride solution in DMSO as solvent.

Figure 5A.14: (a-d) TEM images of [bmim]BF₄ protected cobalt nanoparticles
*Reaction conditions: 0.01M CoCl₂.6H₂O reduced using 0.05M Sodium borohydride solution in DMSO as solvent.
5A.2.5 Electron Diffraction analysis of cobalt NPs

Electron diffraction pattern for the bare and ionic liquid [bmim]BF₄ stabilized cobalt NPs are shown in Figure 5A.15 (a-b) and Figure 5A.16 respectively. The electron diffraction pattern in both the cases shows that the particles are amorphous in nature.

Figure 5A.15: (a-b) Electron diffraction pattern of bare cobalt NPs

* Reaction conditions: 0.01M CoCl₂·6H₂O reduced using 0.05M Sodium borohydride solution in DMSO as solvent.
5A.2.6 Energy-dispersive X-ray (EDAX) analysis of cobalt NPs

EDAX was performed for the synthesized ionic liquid protected cobalt NPs at various regions given in Figure 5A.17 which confirmed the presence of nanoparticle as the elementary component with energy bands centered on 7.5KeV and 0.8KeV corresponding to K and L lines respectively. Rest of the elements like Carbon came from coating over the grid and copper from its base while native oxygen from the atmosphere also appeared.

Figure 5A.16: Electron diffraction pattern for ionic liquid [bmim]BF₄ stabilized cobalt NPs

*Reaction conditions: 0.01M CoCl₂.6H₂O reduced using 0.05M Sodium borohydride solution in DMSO as solvent.

Figure 5A.17: EDAX analysis of ionic liquid [bmim]BF₄ stabilized cobalt NPs.

*Reaction conditions: 0.01M CoCl₂.6H₂O reduced using 0.05M Sodium borohydride solution in DMSO as solvent.
5A.2.7 Scanning Electron Microscopy (SEM) analysis of cobalt nanoparticles.

Scanning Electron microscopic study was carried out to observe the surface morphology of the ionic liquid stabilized cobalt NPs. Sample was prepared by placing a drop of the dispersed solution of the NPs in absolute ethanol over a sterilized glass cover-slip and then drying the latter under a vacuum desiccator. The cover-slip was coated with a metal film for better magnification and then observed under Quanta FEI 200F Scanning Electron Microscope operating at 10000kV. Spherically interlinked array of cobalt NPs could be seen as depicted in Figure 5A.18.

![Figure 5A.18: SEM analysis of ionic liquid [bmim]BF₄ stabilized cobalt NPs](image_url)

*Reaction conditions: 0.01M CoCl₂·6H₂O reduced using 0.05M Sodium borohydride solution in DMSO as solvent.

5A.2.8 VSM (Vibrating Sample Magnetometer) characterization

VSM analysis showing a plot of Magnetization versus Hysteresis (M vs. H) is shown in Figure 5A.19. The ionic liquid stabilized cobalt nanoparticles show no remanent magnetization as shown by magnetization field data. The curve shows a superparamagnetism for these cobalt nanoparticles, a property characteristic of very small ferromagnetic materials (in this case metal particles in the nano-range). Under the influence of thermal energy, small size magnetic moment of the particle as a whole is free to fluctuate and hence, the observed phenomenon.
5A.3 PREPARATIVE METHOD FOR THE SYNTHESIS OF COBALT NPs

The methodology for the preparation of cobalt NPs has been developed, with ILs used as the stabilizing agents. Initially, magnetic stirring was used for carrying out the reduction process but due to presence of external magnetic fields, agglomeration occurred to a large extent. In order to avoid this, ultrasonication was adopted and it was found that agglomeration and coalescence due to an external magnetic force could be largely avoided. Distinguishable by the order of addition of the reagents, two typical possible procedures were adopted for designing the synthetic methodology are as follows:

In a typical procedure 0.01M CoCl$_2$·6H$_2$O in DMSO was taken in a round bottomed flask. To this solution 100µl of ionic liquid was added and the mixture was allowed to stir for at least 15 minutes. To this a homogenized solution of 0.05M sodium borohydride solution in DMSO was added and the reaction vessel was allowed to stand in the water bath of an ultrasonicator operating at 33±3 kHz for 20 minutes at room temperature. Ultrasonic waves led to rapid coalescence and de-coalescence amongst the reacting species which gave the reduced metallic cobalt in the nanometer range. A schematic representation of the procedure is illustrated in Figure 5A.20.
As an alternative method, here the order of addition of reagents was varied a bit. In a typical procedure 0.01M CoCl$_2$.6H$_2$O in DMSO was taken in a round bottomed flask. The reaction vessel was immersed in the water bath of an ultrasonicator operating at 33±3 kHz. Equal volume of 0.05M sodium borohydride solution was added to the same solution drop wise. Immediately after the reduction was over, 100µl of ionic liquid was added as a stabilizer to the reaction mixture so that the formed NPs could be immediately capped by electro-steric stabilization effects. A schematic representation of the procedure is illustrated in Figure 5A.21.
Visual changes in the reaction mixture during the course of synthesis of cobalt nanoparticles from CoCl$_2$.6H$_2$O are shown in Figure 5A.22.

![Visual changes in the reaction mixture during the course of synthesis of cobalt NPs from CoCl$_2$.6H$_2$O](image)

Figure 5A.22: Visual changes in the reaction mixture during the course of synthesis of cobalt NPs from CoCl$_2$.6H$_2$O

It was observed that for the room temperature ionic liquid [bmim]BF$_4$, out of the two methodologies adopted as discussed above, it was found through the DLS measurement studies (Figure 5A.12 (c)) that the second procedure gave better results.

5A.4 CONCLUSION

An efficient method for size controlled synthesis of cobalt NPs with extended stability using an ionic liquid was developed. Optimizing the parameters such as choice of the solvent and the reducing agent concluded DMSO as the solvent of choice while reducing agent concentration could be varied anywhere between three to five times the concentration of the metal ion. ILs could stabilize and destabilize the metal NPs so formed. It was found that it was not only the cationic part of these molten salts, but also the anionic counterpart which played an important role in the stabilization of the NPs. Moreover, the functionality attached in the pendant chain also influenced the stability of the metal NPs. Characterization using various instrumentation techniques such as TEM, SEM, XRD, EDAX, etc. indicated the formation of fine metallic cobalt NPs with a paramagnetic behavior.
REFERENCES


64. Chiappe C, Leandri E, Tebano M. [Hmim][NO3]-an efficient solvent and promoter in the oxidative aromatic chlorination. *Green Chemistry.* 2006;8(8):742-745.
SECTION 5B

Synthesis of copper nanoparticles using chemical reduction method

In this section synthesis of size controlled copper nanoparticles prepared from copper sulphate and using hydrazine hydrate as the reducing agent using a chemical reduction method has been focused upon. Various parameters such as screening of the solvent, selecting the appropriate reducing agent and its concentration, reaction conditions like temperature and pressure were taken into consideration. In order to study the effect of ionic liquid over copper nanoparticles so formed in the chemical reduction process, ILs with their varying cation, anion and functional groups attached were screened in this study. Moreover, the effect of the concentration of room temperature ionic liquid [bmim]BF$_4$ over the size of the copper NPs was looked into. Particles formed were characterized using DLS/QELS, TEM, SEM, UV-Visible, XRD, Selected area electron diffraction and EDAX studies and the results have been discussed.$^1$

\[
\text{CuSO}_4.5\text{H}_2\text{O} + 2\text{N}_2\text{H}_4.2\text{H}_2\text{O} \rightarrow \text{Cu} + \text{N}_2\uparrow + (\text{NH}_4)_2\text{SO}_4 + 9\text{H}_2\text{O}
\]

Scheme 5B.1: Reduction of CuSO$_4$ with Hydrazine hydrate
5B.1 INTRODUCTION

Metal nanoparticles (M-NPs), due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, electronic and sensoric devices, SERS (surface enhanced Raman scattering), catalysis, etc. Copper M-NPs have received considerable attention in the past two decades due to their unusual properties and potential applications in nanomaterials, thermal conducting, lubrication, nanofluids and catalysts. Copper NPs have also presented huge potential for replacing expensive nano silver inks utilized in conductive printing. The major setback that is encountered in utilizing copper NPs is their inherent tendency to get oxidized under ambient conditions and that impedes much of their commercial usability. Reports however suggest that coated or stabilized copper NPs can achieve high conductivities by direct printing of conductive patterns. These approaches open new possibilities in printed electronics. As an example by using copper based inkjet inks operations form various devices such as solar cells, Radio Frequency Identification (RFID) tags and electroluminescence devices can be improved upon.

A number of methods such as microemulsion, reverse micelles, reduction of aqueous copper salts, gamma irradiation, UV light irradiation, polyol process, protecting shells by Pileni et al. and electrolytic techniques by controlling electrode potential have been developed for the preparation of copper nanoparticles. Chen and Sommers have described a one phase system for the synthesis of copper NPs with an alkane thiolate as a protecting monolayer. Sonochemical method and thermal decomposition method have also been reported. However, the copper NPs resulting from these methods had shortcomings, like limited size, monodispersity and susceptibility to oxidation. So there is a crucial need to develop a method to synthesize copper NPs with prolonged stability and in this respect ILs can be developed as a source of potential rescue.

Use of ILs for the synthesis, stabilization and abstraction of metallic and metal based NPs is not new to the field of material chemistry. In this section, the synthesis of copper NPs under optimized conditions of reactants, reducing agent, solvent, reaction conditions like temperature and pressure is being reported and the effect of various ILs over the size of the so formed particles have also been studied. The use of ILs according to DLVO theory (Section 1.9.2) aims at providing electro-steric stabilization to nanoparticles thereby minimizing their closeness leading to agglomeration. Variety of ILs with their varying cations, anions and attached functional groups were studied for their effect over the copper
NPs as synthesized by a wet chemical route. The advantage of the method lies in achieving copper NPs of small sizes in the range less than 50nm and with an extended stability over a period of one year. Particles were extracted out of the reaction mixture and analyzed using various instrumentation techniques for their size, morphology, dispersity and chemical constituents.

5B.2 RESULTS AND DISCUSSION

As per experiments conducted in the previous section for the synthesis of cobalt NPs, solvent system selected here for the synthesis of copper NPs was one which was not capable of reacting with the reducing agent. Reacting the metal salt precursor CuSO$_4$.5H$_2$O with a strong reducing agent sodium borohydride resulted in rapid nucleation and Ostwald ripening leading to agglomeration and very large colloidal particles. However, hydrazine hydrate served to be a mild reducing agent for carrying out the reduction of CuSO$_4$.5H$_2$O to copper nanoparticle. It was observed that the reaction was slow in this case and required certain rate enhancement inputs like an elevated reaction temperature or stabilization of the as formed NPs. When hydrazine hydrate was used as the reducing agent, the solvent employed was the one which could retard the easy oxidation of copper to copper oxide.

In this hunt ethylene glycol and DMSO turned out to be potentially favorable solvents towards the wet chemical synthesis of copper nanoparticles. Both these solvents provided not only a polar medium for the reduction of metal ion but also acted as an efficient dispersing media for the nanoparticulate product formed in the reduction process. However, DMSO was better than ethylene glycol as the latter reacted with hydrazine hydrate leading to complexation and thereby requiring an excess of the reducing agent. In other polar protic solvents, like water, methanol, ethanol, etc. for carrying out the reduction, the problem was easy oxidation of copper to copper oxide. In either of these cases addition of a stabilizer also turned ineffectual.

5B.2.1 Effect of Reducing Agent Concentration

As the redox potential of Cu$^0$/Cu$^{+2}$ is relatively low as compared to metals like gold and silver, the concentration of the reducing agent was one of the most crucial factor which needed to be considered over a broader range. The concentration of the reducing agent (hydrazine hydrate) was varied in the chemical synthesis approach for
synthesis of copper NPs by keeping the concentration of the metal ion to be constant at 0.1M. Reducing agent concentration was explored ranging from 0.1M to 10M. Table 5B.1 depicts the effect of the concentration of hydrazine hydrate as a reducing agent over the size and polydispersity of copper NPs formed from the reduction of 0.1M Cu$^{+2}$ ions using CuSO$_4$.5H$_2$O as the source.

**Table 5B.1: Effect of concentration of reducing agent over size and polydispersity of copper NPs**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Hydrazine hydrate (M)</th>
<th>Size of copper NPs (nm)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B.1.1</td>
<td>10.0</td>
<td>80</td>
<td>0.493</td>
</tr>
<tr>
<td>5B.1.2</td>
<td>9.0</td>
<td>64</td>
<td>0.219</td>
</tr>
<tr>
<td>5B.1.3</td>
<td>8.0</td>
<td>52</td>
<td>1.078</td>
</tr>
<tr>
<td>5B.1.4</td>
<td>7.0</td>
<td>44</td>
<td>3.786</td>
</tr>
<tr>
<td>5B.1.5</td>
<td>5.0</td>
<td>33</td>
<td>0.337</td>
</tr>
<tr>
<td>5B.1.6</td>
<td>3.0</td>
<td>27</td>
<td>0.234</td>
</tr>
<tr>
<td>5B.1.7</td>
<td>2.5</td>
<td>59</td>
<td>0.155</td>
</tr>
<tr>
<td>5B.1.8</td>
<td>2.0</td>
<td>90</td>
<td>0.376</td>
</tr>
<tr>
<td>5B.1.9</td>
<td>1.5</td>
<td>94</td>
<td>0.373</td>
</tr>
<tr>
<td>5B.1.10</td>
<td>1.0</td>
<td>105</td>
<td>0.333</td>
</tr>
<tr>
<td>5B.1.11</td>
<td>0.5</td>
<td>129</td>
<td>0.400</td>
</tr>
</tbody>
</table>

*aReaction conditions: 0.1M CuSO$_4$.5H$_2$O solution in ethylene glycol reduced with varying reducing agent concentrations at room temperature and atmospheric pressure.*
Figure 5B.1: DLS measurement: Effect of reducing agent concentration over the size of copper nanoparticles\(^a\) (a) 0.5M (b) 1.0M (c) 1.5M (d) 2.0M (e) 2.5M (d) 3.0M (f) 5.0M (g) (h) 7.0M (i) 8.0M (j) 9.0 (k) 10.0M indicates reducing agent concentration.

\(^a\)Reaction conditions: 0.1M CuSO\(_4\).5H\(_2\)O solution in ethylene glycol reduced with varying reducing agent concentrations at room temperature and atmospheric pressure.
Data from Table 5B.1 along with the corresponding DLS bar graphs in Figure 5B.1 (a-k) have been summarized in Figure 5B.2. The results and the graph clearly show that the optimum concentration of the reducing agent for reducing 0.01M CuSO₄·5H₂O in ethylene glycol is around 3M. At concentrations below and higher than this, the size of the particles (as measured through DLS studies) increases. At a lower concentration of the reducing agent, the rate of the reduction of the metal precursor is relatively slow and thereby very few nuclei are formed at the stage of nucleation. Precipitating copper atoms at the later period of the reaction lead mostly to particle growth by collision with already generated nuclei rather than in the formation of new particles. This reaction mechanism leads to the formation of larger sized particles.

However, as the concentration of the reducing agent increases, the rate of reduction enhances together with the generation of more nuclei, thereby increasing the population of smaller copper NPs. However, when the concentration of reducing agent goes beyond the stage where all metal ions have been reduced, the rate of nucleation remains constant and the metal clusters start to form with further addition of the reducing agent and the particle size tends to increase.

Figure 5B.2: Variation in size of copper NPs\(^a\) with the increase in reducing agent concentration.

\(^a\)Reaction conditions: 0.1M CuSO₄·5H₂O solution in ethylene glycol reduced with varying reducing agent concentrations at room temperature and atmospheric pressure.
5B.2.2 Effect of Metal ion Concentration

The concentration of the metal salt CuSO$_4$.5H$_2$O was varied from a minimum of 0.025M to a maximum of 0.4M. The concentration of the reducing agent concentration was fixed at 3.0M. Both the solutions were prepared in ethylene glycol. Results as tabulated in Table 5B.2 indicate the effect of increasing the concentration of metal ion on the size of copper nanoparticles. At minimum metal ion concentration, reducing agent was in excess and nuclei formed remained constant in accordance with the bare minimum copper (II) ions present in the reaction mixture. The precipitating atoms tend to accumulate leading to cluster formation and unreacted metal ions underwent complexation with hydrazine hydrate in presence of ethylene glycol thereby just increasing the particle size. As the concentration of metal ion was increased, the concentration of the reducing agent was sufficient enough to reduce all the metal ions and at a particular concentration of metal ion (0.1M in this case, Table 5B.2, Entry 5B.2.4), all nuclei were formed instantaneously with immediate addition of the reducing agent and subsequent growth led to a smaller particle size. As the concentration of metal ion was further increased, the concentration of the reducing agent was inadequate and very few nuclei were produced, which collided with the precipitating metal atoms leading to an increase in the particle size (Figure 5B.3 (a-f), Figure 5B.4).

Table 5B.2: Effect of metal ion concentration over size of copper NPs

<table>
<thead>
<tr>
<th>Entry</th>
<th>CuSO$_4$.5H$_2$O (M)</th>
<th>Size of Copper nanoparticle (nm)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B.2.1</td>
<td>0.5</td>
<td>81</td>
<td>0.392</td>
</tr>
<tr>
<td>5B.2.2</td>
<td>0.4</td>
<td>45</td>
<td>0.203</td>
</tr>
<tr>
<td>5B.2.3</td>
<td>0.2</td>
<td>42</td>
<td>0.472</td>
</tr>
<tr>
<td>5B.2.4</td>
<td>0.1</td>
<td>23</td>
<td>0.140</td>
</tr>
<tr>
<td>5B.2.5</td>
<td>0.05</td>
<td>45</td>
<td>0.151</td>
</tr>
<tr>
<td>5B.2.6</td>
<td>0.025</td>
<td>64</td>
<td>0.310</td>
</tr>
</tbody>
</table>

*Reaction conditions: xM CuSO$_4$.5H$_2$O reduced using 3.0 M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.*
Figure 5B.3: DLS Data: Effect of concentration of metal ion precursor over the size of copper nanoparticles\textsuperscript{a} (a) 0.025M (b) 0.05M (c) 0.1M (d) 0.2M (e) 0.4M (f) 0.5M indicates metal ion concentration.

\textsuperscript{a}Reaction conditions: xM CuSO\(_4\).5H\(_2\)O reduced using 3.0 M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.
Figure 5B.4: Effect of concentration of metal ion precursor over the size of copper nanoparticles

*Reaction conditions: xM CuSO$_4$.5H$_2$O reduced using 3.0 M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.

5B.2.3 Effect of reaction temperature on the synthesis of copper NPs.

As evident in literature, the mode of heating and the rate of heating have been shown to be quite important factors for tuning the size of copper nanoparticles. Microwave heating, oven heating and conventional heating ranging from a lower to a higher temperature in a gradual fashion have been shown to affect the rate of reduction in distinct ways. Greater is the rate of heating, the faster is the nucleation and hence, smaller the particle size. While using ethylene glycol and DMSO as a solvent, an elevation in temperature could cause an increase in the rate of the reduction process leading to a decrease in the particle size (Figure 5B.5, Table 5B.3, Figure 5B.6). It is quite evident that with the increase in reaction temperature to a certain stage, particle size decreased due to acceleration in the rate of reduction and formation of surface active nuclei at a rapid rate (Figure 5B.5a-b, Table 5B.3; Entry 5B.3.1-2). However, beyond that temperature limit these surface active nuclei tend to gain rapid momentum so as to collide under thermal effect and thereby resulting in an increased particle size (Figure 5B.5d-f, Table 5B.3; Entry 5B.3.4-6). Polydispersity index for the copper nanoparticles obtained at the reaction temperature in the range 35°C - 40°C was less than 0.1. It can be evidenced that at the optimum temperature enough nuclei that are formed with an accelerated rate of reduction immediately undergo precipitation to atoms leading a smaller particle size with a narrow nanoparticle size distribution (Figure 5B.5c, Table 5B.3; Entry 5B.3.3).
Figure 5B.5 (a-f): DLS Data of copper nanoparticles formed at different temperatures
(a) 20°C (b) 30°C (c) 35-40°C (d) 50°C (e) 70°C (f) 100°C

*Reaction conditions*: 0.1M CuSO$_4$.5H$_2$O reduced using 3.0 M hydrazine hydrate in ethylene glycol as solvent at varying reaction temperature
Table 5B.3: Effect of the reaction temperature over size of copper nanoparticles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction temperature (°C)</th>
<th>Average Size of copper nanoparticle (nm)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B.3.1</td>
<td>20</td>
<td>52</td>
<td>0.113</td>
</tr>
<tr>
<td>5B.3.2</td>
<td>30</td>
<td>28</td>
<td>0.966</td>
</tr>
<tr>
<td>5B.3.3</td>
<td>35-40</td>
<td>23</td>
<td>0.004</td>
</tr>
<tr>
<td>5B.3.4</td>
<td>50</td>
<td>41</td>
<td>0.205</td>
</tr>
<tr>
<td>5B.3.5</td>
<td>70</td>
<td>151</td>
<td>0.669</td>
</tr>
<tr>
<td>5B.3.6</td>
<td>100</td>
<td>211</td>
<td>0.347</td>
</tr>
</tbody>
</table>

*Reaction conditions:* 0.1M CuSO\(_4\)·5H\(_2\)O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at varying reaction temperature

Figure 5B.6: Effect of reaction temperature on size of copper nanoparticles

*Reaction conditions:* 0.1M CuSO\(_4\)·5H\(_2\)O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at varying reaction temperature

However, carrying the reaction under ultrasonication (Section 5B.3) and stabilizing the particles so formed with room temperature ionic liquid as an additional external stabilizer could avert the use of elevated temperatures for the reduction reaction.

5B.2.4 Influence of ionic liquids over size and polydispersity of copper nanoparticles

Bare copper nanoparticles synthesized using 0.1M CuSO\(_4\)·5H\(_2\)O and 3.0M hydrazine hydrate in ethylene glycol or DMSO as solvent, at room temperature and atmospheric
pressure were prone to rapid agglomeration leading to an increase in particle size. **Figure 5B.8** explains the trend in the size of the copper nanoparticles with the progression in time. The DLS data (**Figure 5B.7**) has been obtained at different time intervals for the copper nanoparticles formed using the standard reaction conditions (as discussed in previous sections). Together with the progression in time, the size first decreased due to the maturation of the already formed nuclei by collision amongst themselves. However, with further increase in time, the size increased because of the maturation of the particles by Ostwald ripening and mutual collision due to high surface activity.

**Figure 5B.7 (a-i):** DLS data for copper nanoparticles isolated from the reaction mixture\(^a\) at different reaction times; (a) 5min (b) 7min (c) 10min (d) 20min (e) 40min (f) 50min (g) 60min (h) 70min (i) 300min.

\(^a\) **Reaction conditions:** 0.1M CuSO\(_4\).5H\(_2\)O reduced using 3M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.
Figure 5B.8: Variation in size of copper nanoparticles with time\(^a\) (without stabilization from an external source)

\(^a\)Reaction conditions: 0.1M CuSO\(_4\).5H\(_2\)O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.

Thus, there aroused a necessary need for stabilization of the so formed copper nanoparticles using an efficient stabilizer. Encouraged by the results obtained for the effect of various ionic liquids over the size of cobalt nanoparticles (Section 5A.2.3), a similar line of experiments were explored, where the effect of a few ionic liquids over the size of copper nanoparticles were observed. These particles were characterized using DLS, TEM, XRD, UV and SEM techniques.

In a typical experiment, 0.01M CuSO\(_4\).5H\(_2\)O solution in ethylene glycol was reduced with 3.0 M hydrazine hydrate for complete reduction, in an ultrasonicator at room temperature and atmospheric pressure. Following complete addition of the reducing agent, 0.1\(\mu\)l addition of ionic liquid or its saturated solution in ethylene glycol was added. Immediately after stabilization, the size of the confined particles was measured using DLS. Figure 5B.9 shows the color of dispersed copper nanoparticles (in ethylene glycol) when stabilized with different ILs. Results have been tabulated in Table 5B.4, in accordance with the DLS data in Figure 5B.10.
Figure 5B.9: Dispersed solution of copper NPs stabilized using different ILs; (a) No ionic liquid (b) [amm]Br (c) [mmor]NO$_3$ (d) [C$_1$COOHmim]Cl (e) [bmim]BF$_4$

*Reaction conditions:* 0.1M CuSO$_4$.5H$_2$O reduced using 3.0 M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.

Figure 5B.10: DLS data copper nanoparticles stabilized with different ILs (a) no ionic liquid (b) [C$_1$COOHmim]Cl (c) [bmim]BF$_4$ (d) [ammor]Br (e) Tetramethylammonium bromide (f) [bmim]Cl (g) [bmmor]BF$_4$ (h) [mmor]NO$_3$.

*Reaction conditions:* 0.1M CuSO$_4$.5H$_2$O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.
Table 5B.4: Effect of ILs over size and polydispersity of copper nanoparticles

<table>
<thead>
<tr>
<th>Entry No</th>
<th>Ionic liquid b (Structure)</th>
<th>Ionic liquid (Name)</th>
<th>Size of Cu-NPs</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B.4.1</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>3.916</td>
</tr>
<tr>
<td>5B.4.2</td>
<td><img src="image1" alt="Structure" /></td>
<td>[C1COOHmim]Cl</td>
<td>Precipitation</td>
<td>-</td>
</tr>
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<td>5B.4.3</td>
<td><img src="image2" alt="Structure" /></td>
<td>[bmim]BF4</td>
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<td>[ammor]Br</td>
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<tr>
<td>5B.4.5</td>
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<td>[Me4N]Br</td>
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<td><img src="image7" alt="Structure" /></td>
<td>[mmor]NO3</td>
<td>18</td>
<td>0.547</td>
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*Reaction conditions: 0.1M CuSO4·5H2O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.

Results in Table 5B.4 illustrate the effect of various ionic liquids over the size of copper NPs. It is evident that the imidazolium cation due to its bulky size and dispersed charge was most efficient in stabilizing the so formed nanoparticles (Table 5B.4; Entry 5B.4.3), giving a mean size of 11nm. Thus, the size of the [bmim]BF4
stabilized particles was found to be smaller by 30nm (compared to the non-stabilized Cu-NPs(\textit{Table 5B.4; Entry 5B.4.1}). Smaller cations like tetramethylammonium ion in [Me₄N]Br led to an increase in the particle size to about 70 nm (\textit{Table 5B.4; Entry 5B.4.5}). Addition of [bmmor]BF₄ also decreased the mean size to 27nm, indicating that the presence of tetrafluoroborate anion (BF₄⁻) was quite beneficiary in terms of electrostatic stabilization (\textit{Table 5B.4; Entry 5B.4.3 and Entry 5B.4.7}). Ionic liquids with chloride anions, however, destabilized the nanoparticles by increasing their size to as high as 79 nm (\textit{Table 5B.4; Entry 5B.4.6}). This could be possible due to inefficient electrostatic stabilization by relatively smaller chloride anion that could not restrict the movement of the particles leading to collision and an increase in the particle size. Morpholinium cation is another suitable candidate which could stabilize the copper nanoparticles resulting in particles size as low as 27 nm and 18 nm (\textit{Table 5B.4; Entry 5B.4.7 and Entry 5B.4.8}). Functionalities like allyl group attached to the morpholinium cation in [ammor]Br gave a decreased particle size of about 34nm (\textit{Table 5B.4; Entry 5B.4.4}), while acetic acid attached to imidazolium cation in [C₅COOHmim][Cl] resulted in solid-liquid phase separation (\textit{Table 5B.4; Entry 5B.4.2}).

5B.2.5 Influence of Ionic liquid concentration

The effect of the concentration of the ionic liquid added to the reaction mixture containing metal nanoparticles seems to be an important aspect to be explored. Effect of the concentration of ionic liquid [bmim]BF₄ was witnessed over the size of copper nanoparticles synthesized from 0.01M CuSO₄.5H₂O using 3.0 M hydrazine hydrate as reducing agent in an ultrasonicator under atmospheric pressure and at room temperature. It was observed (\textit{Table 5B.5 and Figure 5B.11}) that, at the minimum concentration (in this case 0.125M), the ionic liquid was insufficient for effective stabilization of the M-NPs and hence the particles were formed with maximum size and polydispersity. However, with the increase in concentration of ionic liquid up to 0.5M, there was a sharp decrease in the size of the particles. Beyond this concentration, the decrease in particle size became much more gradual. It could be observed that a molar concentration (maximum at 2M) was effective for 100μl addition of ionic liquid.
Table 5B.5: Influence of the concentration of ionic liquid [bmim]BF₄ upon the size of copper NPs \(^a\) (nm)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Concentration of ionic liquid [bmim]BF₄ (M)</th>
<th>Size of Cu-NPs (nm)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B.5.1</td>
<td>0.125</td>
<td>111</td>
<td>0.427</td>
</tr>
<tr>
<td>5B.5.2</td>
<td>0.25</td>
<td>71</td>
<td>0.323</td>
</tr>
<tr>
<td>5B.5.3</td>
<td>0.5</td>
<td>55</td>
<td>0.096</td>
</tr>
<tr>
<td>5B.5.4</td>
<td>1.0</td>
<td>20</td>
<td>0.138</td>
</tr>
<tr>
<td>5B.5.5</td>
<td>1.5</td>
<td>19</td>
<td>0.999</td>
</tr>
<tr>
<td>5B.5.6</td>
<td>2.0</td>
<td>11</td>
<td>0.019</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: 0.1M CuSO₄·5H₂O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.

Figure 5B.11: Influence of the concentration of ionic liquid [bmim]BF₄ upon the size of Cu-NPs \(^a\) (nm)

\(^a\)Reaction conditions: 0.1M CuSO₄·5H₂O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.

5B.2.6 UV-Visible Absorbance Spectrum for Copper Nanoparticles

Figure 5B.12 gives the UV-Visible spectrum for dispersed copper nanoparticles in ethylene glycol. The reaction was carried out using 0.1M CuSO₄·5H₂O and 3.0M hydrazine hydrate in ethylene glycol as solvent at room temperature and atmospheric pressure. The reduced species were stabilized using 2.0M ionic liquid [bmim]BF₄ in
the same solvent. The spectrum shows a characteristic $\lambda_{\text{max}}$ for copper nanoparticles near 580nm. Color of the solution was intense yellow at this stage. Spectrum indicates the formation of pure metallic copper.

**Figure 5B.12**: UV-Visible spectrum of copper nanoparticles\(^a\) stabilized with ionic liquid [bmim]BF\(_4\)

\(^a\text{Reaction conditions: } 0.1\text{M CuSO}_4\cdot5\text{H}_2\text{O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.}\)

**5B.2.7 TEM and SEM characterization for copper nanoparticles**

Transmission electron microscope studies were carried out for copper NPs prepared in ethylene glycol and stabilized with room temperature ionic liquid [bmim]BF\(_4\). The reason behind choosing the ionic liquid for all characterization was the stability of copper NPs rendered by the ionic liquid for an extended time period. In order to prepare the samples for TEM analysis 5mg of isolated and washed copper nanoparticles were dispersed in 25ml of ethanol using an ultrasonicator and this yielded a clear dispersed solution of nanoparticles. 10µl of this solution was dropped over a carbon coated copper grid and the grid was air dried in a vacuum desiccator for few hours. The dried grid was then examined under an electron microscope (TEM TECHNAI 300KV, Ultra twin FEI with EDAX transmission electron microscope operating at 300 kV). **Figure 5B.13 (a-f)** presents TEM images of copper nanoparticles prepared using standard chemical reduction method using 0.01M CuSO\(_4\).5H\(_2\)O using 3.0 M hydrazine hydrate as reducing agent in an ultrasonicator
under atmospheric pressure and at room temperature. TEM images illustrate spherical copper nanoparticles with little agglomeration due to presence of a thin film of ionic liquid surrounding the metal nanoparticles.

Figure 5B.13 (a-f): TEM images of copper nanoparticles\textsuperscript{a} stabilized with ionic liquid [bmim]BF\textsubscript{4}

\textsuperscript{a}Reaction conditions: 0.1M CuSO\textsubscript{4}.5H\textsubscript{2}O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.
SEM characterization was carried out by placing a drop of the dispersed solution of copper nanoparticles in ethanol over a cover-slip and then drying it in vacuum desiccator for few hours. The cover-slip was afterwards coated with a thin metal film for enhanced magnification. Copper nanoparticles stabilized with ionic liquid [bmim]BF$_4$ have been characterized using SEM and images are displayed in Figure 5B.13 (a-c). Particles visualized in these images were irregular to nearly spherical in certain cases.

![SEM images of copper nanoparticles stabilized with ionic liquid [bmim]BF$_4$](image)

*Reaction conditions:* 0.1M CuSO$_4$.5H$_2$O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.

**5B.2.8 XRD Data for the synthesized copper nanoparticles**

XRD pattern for copper nanoparticles is displayed in Figure 5B.15 with 2θ values ranging from 20° to 90°. The XRD pattern shows three characteristic peaks for 2θ values at 44.7°, 51.6° and 76.4° for the respectively marked indices of (111), (200) and (220). These peaks accurately resembled impurity less and oxide less FCC copper phase. The average primary particle size of the copper nanoparticles was calculated from the full width at half maximum (FWHM) of the (111) peaks in the XRD pattern using the Debye-Scherrer equation, resulting in an average primary particle size of about 30 nm.
**5B.2.9 EDAX analysis and electron diffraction pattern of copper nanoparticles**

EDAX analysis of the copper NPs stabilized with ionic liquid [bmim]BF$_4$ has been shown in Figure 5B.16. The analysis confirms copper as the elementary component of the sample placed on the grid. However, the grid being itself made up of copper, this analysis could not be taken as a confirmation for elemental copper and instead the results relied on the XRD pattern (Figure 5B.15). Electron diffraction pattern for these stabilized copper NPs has been shown in Figure 5B.17. The pattern displays that copper nanoparticles bearing a thin film of stabilizer are crystalline in nature.

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**Figure 5B.15: XRD pattern for copper nanoparticles**

* Reaction conditions: 0.1M CuSO$_4$.5H$_2$O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.

**Figure 5B.16: EDAX analysis of copper nanoparticles**

* Reaction conditions: 0.1M CuSO$_4$.5H$_2$O reduced using 3.0M hydrazine hydrate in ethylene glycol as solvent at atmospheric pressure and room temperature.
5B.3 PREPARATIVE METHODOLOGY FOR THE SYNTHESIS OF COPPER NANOPARTICLES

The methodology for the preparation of copper NPs was developed with ionic liquids as the stabilizing agents. Unlike the preparative methodology for cobalt nanoparticles where magnetic stirring induced agglomeration (and sonication could hinder that), in the case of copper NPs it was a little different. Here, the reaction was carried out with ultrasonication and this brought out an accelerated rate of reduction while the reduction carried out using magnetic stirring was comparatively slower. When 0.01M CuSO$_4$·5H$_2$O was reduced using 3.0M hydrazine hydrate as a reducing agent and stabilized using an ionic liquid in an ultrasonicator under atmospheric pressure and at room temperature, the reaction was complete after the ionic liquid addition and this was confirmed by UV-Visible spectra for the absence of peak for Cu$^{+2}$ ions. However, when the same reaction was carried out in magnetic stirrer, the measurement could be done only after seven to ten minutes after the addition of the stabilizer. Thus, the effect of ultrasonication was acceleration of the rate of the reduction reaction.
Based on the order of addition of the reagents, two typical possible procedures which could be adopted for designing the synthetic methodology:

In a typical procedure, 0.01M CuSO\textsubscript{4}.5H\textsubscript{2}O in ethylene glycol was taken in a round bottomed flask. To this solution 100µl of ionic liquid was added and the mixture was allowed to stir for at least 15 minutes. To this homogenized solution 3.0M hydrazine hydrate solution in the same solvent was added and the reaction vessel was allowed to stand in the water bath of an ultrasonicator operating at 33±3 kHz for 20 minutes at room temperature. Ultrasonic waves led to rapid coalescence and de-coalescence amongst the reacting species which gave the reduced metallic copper in the nanometer range. A schematic representation of the procedure is illustrated in Figure 5B.18.

![Figure 5B.18: Schematic representation for the synthesis of Cu NPs\textsuperscript{a}](image)

\textsuperscript{a}Reaction conditions: 0.1M CuSO\textsubscript{4}.5H\textsubscript{2}O in ethylene glycol treated with 100 µl of ionic liquid followed by 3.0M hydrazine hydrate solution

In an alternative method, the order of addition of the reagents was varied a bit. In a typical procedure 0.01M CuSO\textsubscript{4}.5H\textsubscript{2}O in ethylene glycol was taken in a round bottomed flask. The reaction vessel was immersed in the water bath of an ultrasonicator operating at 33±3 kHz. Equal volume of 3.0M hydrazine hydrate solution was added to the same solution drop wise. Immediately after the reduction was over, 100µl of ionic liquid was added as stabilizer to the reaction mixture such that the formed nanoparticles were immediately capped by electro-steric stabilization effects. A schematic representation of the procedure is illustrated in Figure 5B.19.
µydrazine hydrate (Dropwise addition)

CuSO₄.5H₂O in DMSO or ethylene glycol

Figure 5B.19: Schematic representation for the synthesis of Cu NPs

Reaction conditions: 0.1M CuSO₄.5H₂O in ethylene glycol treated with 3.0M hydrazine hydrate solution followed by 100 µl of ionic liquid

5B.4: CONCLUSION

- The experimental and observational studies in this section illustrated a simple and convenient method of preparing copper nanoparticles in the absence of an inert atmosphere with rate initiation inputs like ultrasonication.

- Unlike previously reported methods for the synthesis of copper nanoparticles, here conversion of metallic cobalt to its oxide could be prevented by stabilization with a variety of room temperature ionic liquids.

- Effect of ionic liquid in stabilizing a particular metal nanoparticle depends upon the intrinsic make up of the ionic liquid which is characterized by its distinct cation, anion or any other attached functionality.

- Concentration of the reducing agent and the metal ion are important factors to be considered for reaching over an optimized method for synthesizing copper nanoparticles.
REFERENCES


SECTION 5C

Synthesis of ionic liquid stabilized silver nanoparticles using chemical reduction method

Imidazolium and morpholinium based ionic liquid stabilized silver nanoparticles were synthesized using wet chemical synthesis employing hydrazine hydrate as the reducing agent and DMSO as a solvent at room temperature and atmospheric pressure. Crystalline silver nanoparticles, spherical in shape and small in size (in the range of 3 nm–16 nm), were synthesized and characterized using DLS, UV-Visible, TEM, SEM, SAED, EDAX and XRD studies.

\[ 2\text{AgNO}_3 + 3\text{NH}_2\text{NH}_2.2\text{H}_2\text{O} \rightarrow 2\text{Ag} + 4\text{N}_2\uparrow + 12\text{H}_2\text{O} \]

Scheme 5C.1: Reduction of AgNO\(_3\) using hydrazine hydrate
5C.1 INTRODUCTION

Silver nanoparticles have attracted considerable interest because of their unique characteristics. They are electrically conductive, can function as catalysts and exhibit a surface-enhanced Raman effect as well as an antibacterial effect. Because of their antimicrobial effect, silver nanoparticles have been applied to a wide range of healthcare products, such as burn dressings, scaffolds, water purification systems and medical devices.

Chemical reduction is one of the most frequently applied method for the preparation of silver nanoparticles as stable, colloidal dispersions in water or organic solvents using commonly used reductants such as borohydride, citrate, ascorbate and elemental hydrogen. In green synthesis approach of synthesizing silver nanoparticles, polysaccharides, polyoxometalates, Tollén’s reagent, biological methods, irradiation methods have been used. Ionic liquids have assisted a variety of inorganic material synthesis because of their unique properties. Applicability of pyrolidium and imidazolium based ionic liquids towards the synthesis of silver nanoparticles has been cited by various researchers. 1-butyl,3-methylimidazolium ([bmim]) cation has been frequently used in thermal and electrochemical processes for the reduction of appropriate silver salt to colloidal silver. Bis-alkyl and hydroxyl functionalized imidazolium ionic liquids have also been used by different workers. Effect on morphological properties of silver nanoparticles has been studied by Suh et al. upon varying counter anions like tetrafluoroborate, methylsulphate, chloride and bromide in 1-butyl,3-methylimidazolium cation.

1-(dodecyl)-2-amino-pyridiniumbromide ionic liquid has also been used in a one phase method for the synthesis of uniform, mono-dispersed and crystalline silver nanoparticles in water-ionic liquid system using an excess of hydrazine hydrate as the reducing agent. Most of the methods used till date to synthesize silver nanoparticles using ionic liquids have either utilized elevated temperature conditions, long reaction times and have shown low yields. The method described in this section, uses ultrasonic irradiation for the synthesis of silver nanoparticles using hydrazine hydrate as the reducing agent at room temperature and atmospheric pressure in DMSO as solvent and ionic liquid as stabilizers. Reaction goes to completion within minutes and the particles are formed with an extended stability period unlike particles isolated from conventional methods. The literature mentions about sonochemical synthesis of silver
nanoparticles, where sodium borohydride and sodium citrate have been used for size controlled synthesis of silver nanoparticles, but the method lacks the provision for stabilizing the so formed particles with a suitable agent.\textsuperscript{24}

**5C.2 PREPARATIVE METHOD FOR SILVER NANOPARTICLES IN DMSO USING IONIC LIQUIDS AS STABILIZERS**

Reducing agent opted for the reduction of silver nitrate to silver metal in colloidal state was hydrazine hydrate. Sodium borohydride being a stronger reducing agent is known to give large size particles. On the contrary sodium citrate and glucose (or rests of the sugars) give polydispersed particles. Preparative method for silver nanoparticles using ultrasonication has been found to be very efficient in terms of yield and time required for the reduction process. In a typical reaction, a flask containing 10mM solution of AgNO$_3$ in DMSO was immersed in water bath of an ultrasonicator operating at 33$\pm$ 3 kHz at room temperature. This was followed by drop wise addition of 10.5mM solution of hydrazine hydrate into the metal ion solution. 100µl of ionic liquid was added immediately in neat form or its saturated solution in DMSO. Solution was further sonicated for additional five minutes where nucleation was followed by precipitation and immediate electro-steric stabilization of the particles so formed in ionic liquid-DMSO system. Figure 5C.1 represents the diagrammatic scheme for the synthesis of silver nanoparticles in chemical reduction (Scheme 5C.1) using ionic liquids as stabilizers.

![Figure 5C.1: Schematic representation for the synthesis of silver nanoparticles\textsuperscript{a}\textsuperscript{a}](image)

\textsuperscript{a}\textbf{Reaction conditions:} 10 mM AgNO$_3$ in DMSO treated with 10.5 mM hydrazine hydrate solution followed by 100 µl of ionic liquid.
Chapter 5

5C.3 RESULTS AND DISCUSSION

5C.3.1 Effect of ionic liquid in synthesis of silver nanoparticles

In this section a comparison was derived between silver nanoparticles synthesized in the presence and absence of ionic liquids. When 10mM solution of AgNO₃ was reacted with equal volume of 10.5mM hydrazine hydrate in an ultrasonicator at room temperature and atmospheric pressure the color of the solution turned yellow, indicating the formation of silver nanoparticles (Figure 5C.2 (a)). Through DLS study the size of the dispersed silver nanoparticles formed under these conditions was found to be about 14nm (Figure 5C.2 (b-c)).

![Figure 5C.2(a): Silver nanoparticles formed without addition of a stabilizing agent (b,c) DLS data for the silver nanoparticles formed without capping.](image)

*Reaction conditions: 10mM AgNO₃ reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure.*

Ionic liquids derived from methylimidazole and methylmorpholine were used to study their effect over the size of silver nanoparticles. Ionic liquid was added immediately after the addition of reducing agent to the reaction mixture so that the metallic nanoparticles in the dispersed state could be isolated as capped nanoparticles. Figure 5C.3 (a-e) presents the photographic images of silver nanoparticles stabilized with different ionic liquids. The results for the addition of various ionic liquids in their respective reaction sets are populated in Table 5C.1 and these are in accordance with the DLS data in Figure 5C.4 (a-g).
Figure 5C.3: Photographic images of silver nanoparticles stabilized using different ionic liquids; (a) [C$_1$COOHmim]Cl (b) [bmim]BF$_4$ (c) [ammor]Br (d) [Me$_4$N]Br (e) [bmmor]BF$_4$

*Reaction conditions:* 10mM AgNO$_3$ reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure and stabilized using ionic liquid.
Figure 5C.4: DLS images for silver nanoparticles prepared using ionic liquids; (a)[C$_1$COOHmim]Cl (b)[bmim]BF$_4$ (c)[ammor]Br (d)[Me$_4$N]Br (e)[bmim]Cl (f)[bmmor]BF$_4$ (g)[mmor]NO$_3$.

*Reaction conditions: 10mM AgNO$_3$ reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure and stabilized using ionic liquid.
Table 5C.1: Effect of Imidazolium and Morpholinium ILs on the size of silver nanoparticles\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry No</th>
<th>Ionic liquid \textsuperscript{b} (Structure)</th>
<th>Ionic liquid (Name)</th>
<th>Size of silver nanoparticles (nm)</th>
<th>Polydispersity</th>
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</thead>
<tbody>
<tr>
<td>5C.1.1</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>0.588</td>
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<td>5C.1.2</td>
<td><img src="image1" alt="Structure" /></td>
<td>[C\textsubscript{1}COOHmim]Cl</td>
<td>05</td>
<td>1.318</td>
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<tr>
<td>5C.1.3</td>
<td><img src="image2" alt="Structure" /></td>
<td>[bmim]BF\textsubscript{4}</td>
<td>05</td>
<td>1.390</td>
</tr>
<tr>
<td>5C.1.4</td>
<td><img src="image3" alt="Structure" /></td>
<td>[ammor]Br (Turbid yellow solution)</td>
<td>02</td>
<td>2.196</td>
</tr>
<tr>
<td>5C.1.5</td>
<td><img src="image4" alt="Structure" /></td>
<td>Tetramethylammonium bromide</td>
<td>7.0</td>
<td>1.756</td>
</tr>
<tr>
<td>5C.1.6</td>
<td><img src="image5" alt="Structure" /></td>
<td>[bmim]Cl</td>
<td>09</td>
<td>0.038</td>
</tr>
<tr>
<td>5C.1.7</td>
<td><img src="image6" alt="Structure" /></td>
<td>[bmmor]BF\textsubscript{4}</td>
<td>02</td>
<td>-</td>
</tr>
<tr>
<td>5C.1.8</td>
<td><img src="image7" alt="Structure" /></td>
<td>N-methylmorpholinium nitrate or [mmor]NO\textsubscript{3}</td>
<td>14</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 10mM AgNO\textsubscript{3} reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure and stabilized using ionic liquid.
Results indicated that the size of the silver NPs could be largely affected by the presence of ILs. As shown in Figure 5C.2 the size of the particles was around 14 nm, however on stabilization with ILs, color of the solution changed (Figure 5C.3 (a-e)) and the size showed a major dip (Figure 5C.4 (a-g)). It could be seen that both the imidazolium and morpholinium based ILs were responsible in controlling the size of the nanoparticles in the range of 2nm to 5nm. It must be emphasized that both the allyl functionality (Table 5C.1; Entry 5C.1.2) and acetic acid functionality (Table 5C.1; Entry 5C.1.4) greatly affected the size of the metal nanoparticles. It was also found that nitrate anion ([mmor]NO$_3$) did not help in affecting the size much (Table 5C.1; Entry 5C.1.8).

All other ILs from the family gave small sized and stable nanoparticles. Table 5C.2 indicates the extended stability of silver NPs with time for the ionic liquid [ammor]Br. Figure 5C.5 shows the trend in size of silver NPs with time. Increase in the size of the nanoparticles was gradual even after days of performing the reaction. It was clear that the ionic liquid stabilized silver nanoparticles could be stored and used for subsequent studies or applications.

Table 5C.2: Effect of time on size of ionic liquid stabilized silver nanoparticles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time of DLS study</th>
<th>Size of Ag np (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5C.2.1</td>
<td>5 min</td>
<td>02</td>
</tr>
<tr>
<td>5C.2.2</td>
<td>1 day</td>
<td>02</td>
</tr>
<tr>
<td>5C.2.3</td>
<td>3 days</td>
<td>02</td>
</tr>
<tr>
<td>5C.2.4</td>
<td>8 days</td>
<td>03</td>
</tr>
<tr>
<td>5C.2.5</td>
<td>30 days</td>
<td>03</td>
</tr>
</tbody>
</table>

*Reaction conditions: 10mM AgNO$_3$ reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure and stabilized using ionic liquid [ammor]Br.
Figure 5C.5: Effect of time on size of ionic liquid stabilized silver nanoparticles

*Reaction conditions:* 10mM AgNO<sub>3</sub> reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure and stabilized using ionic liquid [ammon][Br].

5C.3.2 TEM and SEM studies for silver NPs

Transmission electron microscopic (TEM) studies were carried out for the silver nanoparticles stabilized with ionic liquid. **Figure 5C.6 (a-f)** shows images of silver nanoparticles synthesized in DMSO as a solvent and stabilized with the room temperature ionic liquid [bmim]BF<sub>4</sub> under the standard reaction conditions chosen for synthesis of silver NPs throughout. Particles were spherical in shape and showed fringes indicating crystalline nature of the metallic particles. These images were in accordance with the DLS data (**Figure 5C.4 (b)**) with particle sizes less than 10 nm range. **Figure 5C.7 (a-d)** shows SEM images for silver nanoparticles. Scanning electron microscopic studies also confirmed the spherical nature of the particles. Stabilization of M-NPs by ILs in presence of polar aprotic solvent DMSO illustrates the stabilization of the induced charge on the particle surface when they come closer.
Figure 5C.6: TEM images of silver nanoparticles stabilized with ionic liquid [bmim]BF₄

*Reaction conditions:* 10mM AgNO₃ reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure.
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Figure 5C.7: SEM images of silver nanoparticles\textsuperscript{a} stabilized with ionic liquid [bmim]BF\textsubscript{4}

\textsuperscript{a}Reaction conditions: 10mM AgNO\textsubscript{3} reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure.

5C.3.3 Selected Area Electron Diffraction pattern and EDAX analysis of Silver Nanoparticles

Electron diffraction pattern for silver NPs has been shown in Figure 5C.8. The pattern corresponds to that of crystalline silver NPs. It can be postulated that stabilization of the M-NPs by a thin film of ionic liquid is favorable compared to synthesizing them in an ionic liquid media alone. Energy dispersive X-ray analysis of silver NPs (Figure 5C.9) shows elemental silver as the major component of the material placed on the copper grid.
**Figure 5C.8**: Selected area electron diffraction pattern of silver NPs\(^a\) stabilized with ionic liquid [bmim]BF\(_4\)

\(^a\)**Reaction conditions**: 10mM AgNO\(_3\) reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure.

**Figure 5C.9**: EDAX analysis of silver NPs\(^a\) stabilized with ionic liquid [bmim]BF\(_4\)

\(^a\)**Reaction conditions**: 10mM AgNO\(_3\) reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure.
5C.3.4 XRD Studies for ionic liquid stabilized silver nanoparticles

X-ray diffraction analysis of the powdered sample of silver NPs is displayed in Figure 5C.10 with 2θ values ranging from 20° to 100°. The XRD pattern shows five characteristic peaks for 2θ values at 38.8°, 45.2°, 65.1°, 76.7° and 81.8° for the respectively marked indices of (111), (200), (220), (311) and (222). The pattern validates the face centered cubic structure of silver NPs. The average primary particle size of the copper nanoparticles was calculated from the full width at half maximum (FWHM) of the (111) peaks in the XRD pattern using the Debye-Scherrer equation, resulting in an average primary particle size of about 19 nm.

![Figure 5C.10: XRD analysis of silver NPs stabilized with ionic liquid [bmim]BF₄](image)

*Reaction conditions:* 10mM AgNO₃ reacted with 10.5mM hydrazine hydrate in DMSO using ultrasonic irradiation at room temperature and at atmospheric pressure. Particles isolated and dried in vacuum.

5C.3 CONCLUSION

Ionic liquid stabilized silver NPs with size ranging between 2 nm - 5 nm have been synthesized using the chemical reduction method initiated by ultrasonication. Small sized and crystalline silver nanoparticles could be synthesized using hydrazine hydrate as reducing agent and an ionic liquid as the stabilizer. It has been found that ionic liquid based on morpholinium cation gave the smallest silver nanoparticles in the size range of 2 nm – 3 nm. Ionic liquids with different cationic and anionic constituents differently stabilized the metal nanoparticles.
REFERENCE


