APPENDIX

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4. Pushpa R Gopalan, A.G. Annaselvi and P. Subramaniam, Spectroscopic study of bifenox complexation with α-, β- and γ-cyclodextrin in solution and in the solid state, Communicated to *Journal of Molecular structure*.


SYNTHESIS AND CHARACTERIZATION OF β-CYCLODEXTRIN CAPPED SILVER NANOPARTICLES

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Received 03 March 2013; accepted 14 March 2013

Abstract
The present study deals with the synthesis of silver nanoparticles (AgNPs) using β-Cyclodextrin as the reducing agent. The typical synthesis of gold and silver nanoparticles incorporates contaminants that could pose problems. Here we describe cost effective and environment friendly techniques for green synthesis of silver nanoparticles from AgNO₃ solution and β-Cyclodextrin as reducing as well as capping agent. Thermal treatment has been used to intensify the reduction. The optimum condition for obtaining silver nanoparticles was at pH11. The formation of AgNPs was confirmed by UV-Visible Spectroscopy, X-Ray Diffraction (XRD) pattern and Transmission Electron Microscopy (TEM). The synthesized AgNPs were predominately spherical in shape and poly dispersed. The particles were stable for at least 4 months at a temperature of 25°C.

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Keywords: Silver nanoparticles, β-Cyclodextrin, TEM and XRD

1. Introduction
The field of nanotechnology is one of the most active areas in science. Over the past decade, silver nanoparticles have stimulated great interest because of their applications in biomedicine, sensing and catalysis. Some biomolecules have been introduced as environmentally friendly reducing and capping agents for the synthesis of noble metal nanoparticles. Wallen and co-workers [1] have successfully synthesized starched silver nanoparticles in the size range of 1-8 nm by gently heating an aqueous solution of silver nitrate, soluble starch and glucose, where glucose served as an environmentally benign reducing agent and starch provided stable surface passivation or protection. Nanoparticles of metals play important roles in different fields. They have been investigated extensively in recent years due to their properties which differ from the bulk substances [2]. Nanoparticles possess a very high surface to volume ratio. This can be utilized in areas where high surface areas are critical for success. The applications of nanoscale materials like solar energy conversion, catalysis, medicine and water treatment are depending on their size, shape and chemical surroundings [3]. The noble metals, especially silver and gold, have attracted great attention due to their innumerable applications, which are useful in areas of photography, catalysis, biological labeling, photonics, and optoelectronics and as antimicrobial agents. Metal nanoparticles can be synthesized and stabilized through chemical and mechanical methods [4, 5], electrochemical techniques [6], photochemical reactions in reverse micelles [7] and nowadays via green chemistry method [8]. Synthesis of metal nanoparticles and study of their size and properties are of fundamental importance in the advancement of recent research [9]. Recently, gold nanoparticles with size of 10 nm have been successfully synthesized by employing D-glucose as both reducing agent and capping agent under controlled pH environments [10]. Stabilization using β-Cyclodextrin in the synthesis of mono and bimetallic nanoparticles in alkaline solution has been explored [11]. However, it remains a challenge to develop facile and environmentally friendly methods for the feasible synthesis of silver nanoparticles with controlled size, shape and surface functionality. The nanoscale materials of platinum, palladium, gold and silver can be used in the development of a new generation catalytic and sensing devices. Of great environmental concern is the fact that nanoparticles can enter human body through lungs and...
intestinal tract and to a lesser extent through skin and are likely to be a health issue; although the seriousness of the effects is inconclusive. Hence it becomes more imminent to synthesize nanomaterials through greener and less hazardous methods. One such method for the synthesis of metal nano particle is the simple reduction of metal chlorides and nitrates in to metal nanoparticles by aminoacids in the presence of aqueous β-Cyclodextrin(CD)as capping agent.[12].This method is not only simple but also eco-friendly as it is devoid of any hazardous reducing agents and their disposal. As a class of water-soluble and nontoxic cyclic oligosaccharides with a hydrophilic exterior and a hydrophobic interior, cyclodextrins (CDs) have been extensively investigated in host-guest chemistry. They can form inclusion complexes incorporating various molecular guests within their hollow, truncated cone-shaped cavity structure, enabling them to be used as drug carriers, enzyme mimics and for construction of versatile supramolecular aggregations owing to their special hydrophobic cavities [13, 14]. CDs too induce nanoparticle assembly via host-guest interactions because of their relatively weak capping ability for metal nanoparticles. Although the hydroxylic groups are poor electron donor ligands to silver, in relatively high concentrations, β-cyclodextrin is able to stabilize AgNPs. Herein, we report the controlled synthesis of silver nanoparticles by directly reducing silver nitrate with β-CD in an alkaline aqueous solution. The bio reduction behavior of β-CD in the synthesis of silver nanoparticles was investigated employing UV/visible Spectrophotometry, X-ray diffraction (XRD), and transmission electron microscopy (TEM).

2. Materials and Methods

2.1 Materials.
Silver nitrate (Merck) and β- Cyclodextrin (Himedia) were the chemicals purchased of high purity grade. All the samples were used without any further treatment. All solutions were freshly prepared each time, using doubly distilled water.

2.2 Synthesis of β-CD-Capped Ag Nanoparticles.

The synthesis of β-CD-capped Ag nanoparticles was simply achieved by the reduction of silver nitrate with β-CD in alkaline aqueous solution. Working solution of silver nitrate with concentration 10⁻¹ M was prepared from stock solution of 10⁻² M in doubly distilled water. An aqueous solution of β- Cyclodextrin was prepared such that its concentration was about 15 times higher than silver nitrate solution which was added and stirred for about 10min. Then sodium hydroxide solution was added and magnetically stirred continuously until silver ions were reduced to silver metal in nano dimensional range. During reduction process the temp was kept at 30- 35°C.

2.3 Sample Characterization

The products were characterized by X-ray diffraction (Rigaku Dmax-2000, Ni-filtered Cu KR radiation), UV-visible Spectrophotometry with Jasco -550 double-beam spectrophotometer and Transmission electron microscope (TEM Philips CM20).

3. Results and Discussion

3.1 X-Ray Diffraction Studies

X-ray diffraction is one of the most important characterization tools used in Solid State Chemistry and Material Science. XRD is an easy tool to determine the size and the shape of the unit cell for any compound. The dried mixture of AgNPs was collected for the determination of the formation of AgNPs by an X-ray diffractometer. The crystallite domain size was calculated from the width of the XRD peaks, assuming that they are free from non-uniform strains, using the Scherer’s formula:

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]

Where D is the average crystallite domain size perpendicular to the reflecting planes, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction angle. To eliminate additional instrumental broadening, the FWHM was corrected using the FWHM from a large grained Si sample:

\[ \beta \text{ corrected} = (\text{FWHM' sample} - \text{FWHM' Si})^{1/2} \]

This modified formula is valid only when the crystallite size is smaller than 100 nm.[15] The XRD study indicates that the resultant particles are (FCC) silver Nanopowder. The obtained results illustrate that silver ions had indeed been reduced to Ag⁺ by β- Cyclodextrin under reaction conditions. A number of Bragg reflections corresponding to the (111), (200), and (220) sets of lattice planes are observed which may be indexed based on the face centered cubic (FCC) structures of silver. Peaks were also observed suggesting that the crystallization of bio-organic phase occurs on the surface of the silver nanoparticles[16].

Particle Size Calculation

From this study, considering the peak at degrees, average particle size has been estimated by using Debye-Scherrer formula

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

Where ‘λ’ is wave length of X-Ray (0.1541 nm), ‘β’ is FWHM (full width at half maximum), ‘θ’ is the diffraction angle and ‘D’ is particle diameter size. The calculated particle size details are in Table.1. The particle size is less than 50 nm.

Table1: The grain size of silver nanopowder

<table>
<thead>
<tr>
<th>θ of the intense peak (deg)</th>
<th>hkl</th>
<th>θ of the intense peak (deg)</th>
<th>FWHM of Intense peak (β) radians</th>
<th>Size of the particle (D) nm</th>
<th>d-spacing nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>111</td>
<td>19</td>
<td>0.0035</td>
<td>43.9</td>
<td>0.2368</td>
</tr>
<tr>
<td>44.21</td>
<td>200</td>
<td>22.105</td>
<td>0.0033</td>
<td>46</td>
<td>0.2049</td>
</tr>
<tr>
<td>64.3</td>
<td>220</td>
<td>32.15</td>
<td>0.0052</td>
<td>36</td>
<td>0.1447</td>
</tr>
</tbody>
</table>
The formation of cyclodextrin capped silver nano particles is confirmed by X-ray diffractometry. The X-ray spectrum of the cyclodextrin capped silver nano particle shown in Fig.1b was evidently different from that of β-CD monomer itself shown in Fig.1a. The difference between both spectra of β-CD and capped nanoparticle is due to the interaction of β-CD with silver nanoparticle. X-ray diffraction showed the presence of the peaks at 2θ values of 38°, 44.21° and 64.3° corresponding to cubic phase of silver metal.

3.2 UV/Vis Spectroscopy analysis

UV-visible spectroscopy is one of the most widely used techniques for structural characterization of silver nanoparticles. The absorption spectrum (Fig. 2) of the pale yellow-brown silver colloid prepared by β-CD reduction showed a surface Plasmon absorption band with a maximum of 420 nm indicating the presence of spherical or roughly spherical Ag nanoparticles and TEM imaging confirmed this. In metal nanoparticle such as silver, the conduction band and valence band lie very close to each other. The reaction mixture, showed color change from yellowish brown to reddish brown which indicated the formation of silver nano particles. The absorption peak obtained in the visible range 420nm wavelength is a clear evidence of formation of silver nanoparticles from the metal nitrate solution. The frequency and width of the surface Plasmon absorption depends on the size and shape of the metal nanoparticles as well as on the dielectric constant of the metal itself and the surrounding medium [17-19].

3.3 TEM imaging of the sample

A drop of the dilute suspension was placed on a copper grid. The grid was allowed to dry under ambient condition for 24 hours and then vacuum dried. The samples were imaged on a transmission electron microscope. The size and shape of the aggregates were characterized by electron microscopy. Fig 3 shows the TEM micrographs of silver nano particles. In presence of β-CD, silver nanoparticles are nearly spherical and their average size is about 50 nm. Yet there are a few silver crystallites of size100nm and 200 nm, visible in the sample. These images suggest that the particles are poly disperse and are mostly spherical in shape. Hence it may be understood that the experimental conditions (viz., pH, temperature and the optimum concentration of Ag+ etc.) influence dispersity and shape. A few agglomerated nanoparticles were also observed in some places, thereby indicating possible sedimentation at a later time. It is evident that there is variation in particle sizes and the average size estimated was 50 nm for AgNPs.
The torroidal hydrophobic cavity of β-CD is able to have inclusion effects on the silver nitrate in aqueous solution. The interactions such as Vander Waals force and hydrophobic interaction between guest and host are generally accepted as the driving force for the bonding of guest molecules or ions to CD cavity. Nanoparticles with high surface area remain separated from each other. Thus the interactions between silver nitrate and β-CD are important factors responsible for the production of weakly agglomerated and uniformly dispersed silver nanoparticles. The aggregation of the capped nanoparticles is probably driven by both hydrophobic effect and the hydrogen bonding on the capping agent used for the nanoparticle preparation. Proteins can also bind nanoparticles either through free amine groups and therefore, stabilization of the AgNPs and AuNPS by protein is a possibility [20-23]. The biological molecules could possibly perform dual functions of formation and stabilization of silver and gold nanoparticles in the aqueous medium. In this work β-CD was used as the bio-substitute for proteins. This simple procedure for the biosynthesis of silver nanoparticles has several advantages such as cost-effectiveness, compatibility for biomedical and pharmaceutical applications etc.

4. Conclusions

The stabilization of metal Nanoparticles is a challenging issue as the high surface energy of the metal nanoparticle tends to aggregate them into bigger clusters. The consecutive particle growth due to the mutual coalescence between nanoclusters and their neighboring free silver atoms was limited in the presence of CDs. This work offers a reliable protocol for the synthesis of Cyclodextrin capped silver nanoparticles. Characterization using various techniques such as TEM, X-ray diffraction and UV-visible spectrophotometry also provide valuable information about the nanoparticles synthesized by this ‘Green’ facile method. XRD study showed the face-centered cubic lattice of AgNPs. The average crystal size of AgNPs was also found to be 50 nm. TEM analysis of the nanoparticles showed spherical clusters with diameter 50 nm. TEM analysis revealed that the synthesized nanoparticles were stable in solution over a period of 1 month at room temperature. The UV-Visible spectrum reveals the formation of silver nanoparticles by showing surface Plasmon resonance at 420 nm. The significant reduction in reaction time with β-CD is an important result and will enable nanoparticle biosynthesis methods to compete with other routes for the formation of nanoparticles that are currently much more rapid and reproducible. This result provides a very simple and “green” route to uniform CD functionalized Ag nanoparticles, which is potentially extendable to the controlled synthesis of other kinds of metal nanoparticles with specific surface functionality. The obtained uniform Ag nanoparticles functionalized by CD molecules would find a wide range of biomedical applications by virtue of the biologically compatible characteristic as well as the special inclusion ability of the CD molecules. Cyclodextrins synthesized from starch are proved to be the ‘Green Alternatives’ for polymers which are the commonly used as capping agents in nanoparticle synthesis. Cyclodextrins, harmless and easily disposable, play a dual role in this method as reducing agent and capping agent.

5. References


Source of support: Nil; Conflict of interest: None declared
ISSN 2249-8516

Original Article

PREPARATION AND CHARACTERIZATION OF INCLUSION COMPLEXES OF ISOPROTURON WITH NATIVE AND MODIFIED β-CYCLODEXTRINS

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Received 12 November 2012; accepted 19 December 2012

Abstract

The widely used herbicide isoproturon (3-(4-isopropylphenyl)-1, 1-dimethylurea) has a setback in its poor solubility profile. Poor aqueous solubility and slow dissolution of isoproturon result in poor bioavailability. Inclusion complex formation of isoproturon with β-Cyclodextrin (β-CD) and Hydroxy propyl β- Cyclodextrin (HPβ-CD) resulted in stability and solubility enhancement of the herbicide. Complexation was proved by UV-Vis, FT-IR, ¹H NMR and XRD studies. The interaction of isoproturon with β-CD and HPβ-CD is conducive to the formation of inclusion complexes in aqueous as well as in the solid state. A comparative analysis was made on the binding behaviour of isoproturon with β-CD and HPβ-CD and the mode of inclusion of the guest molecule into the host cavities was also envisaged. Inclusion complexes with Guest: Host ratios as 1:2 were also prepared with β-CD and HPβ-CD. Compared to complexes having 1:1 Guest: Host ratio, the complexes having 1:2 G: H ratio displayed better dissolution rates of isoproturon. Therefore, a suitable dosage form incorporating these complexes might show improvement in bioavailability of isoproturon.

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Key words: inclusion complex; Cyclodextrins; Herbicide; Solubility; Isoproturon.

1. Introduction

Cyclodextrins possess a unique torroidal molecular architecture with a hydrophilic exterior and a hydrophobic interior. Cyclodextrins can complex with a broad spectrum of guest molecules of appropriate size, shape and polarity. The physicochemical characteristics of guest molecules are beneficially modified after inclusion into these elegant organized assemblies. In the galaxy of Cyclodextrin inclusion complexes, drug-CD formulations are very significant and important because of the enhanced solubility, bioavailability and stability of drug molecules after inclusion into the hydrophobic cavity of CDs. Structural characterization is of particular significance for these supramolecular host-guest complexes, which are the basis of most CD applications in medicine, catalysis, food chemistry and sensor technology [1-6]. In pesticide formulations the same effects can be achieved as in drug-CD formulations. Isoproturon is a systemic herbicide used for the control of grasses and weeds [7]. It is mobile in soil and persistent in water. It hydrolyses slowly in water with a half-life of thirty days [8]. Isoproturon has a poor water solubility of 72 mg/litre at 20°C which can be improved by inclusion complex formation with β-CD and its derivatives [9]. Poor aqueous solubility and slow dissolution of isoproturon result in poor bioavailability. We have focused on the binding behaviors of β-CD and HPβ-CD with isoproturon and the solubilization effect of β-CD and HPβ-CD toward isoproturon, as these may provide a useful approach to produce isoproturon formulations with high bioavailability. Figure 1 depicts the structure of isoproturon. The carbonyl group in isoproturon is conducive for intermolecular hydrogen bond formation with the hydroxyl groups at the rim of the Cyclodextrin molecule. This factor thus enhances the ability of isoproturon to get included in the hydrophobic cavity of Cyclodextrins. Also the herbicide molecule as shown in Fig 1 possesses non-polar methyl groups at both ends making the inclusion process smooth and comfortable.
ISSN 2249-8516

Original Article

STUDIES ON THE PREPARATION AND CHARACTERIZATION OF \(\beta\)-CYCLODEXTRIN-
PICRIC ACID INCLUSION COMPLEXES

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Received 19 June 2013; accepted 06 July 2013

Abstract

The objective of the present work is to analyze the effect of Beta Cyclodextrin (\(\beta\)-CD) on the absorption spectra of picric acid (PA) in buffer solutions of different pH values 4 and 9. The study reveals that in both pH, PA forms 1:1 inclusion complex. Complexes of PA with \(\beta\)-CD of 1:1 and 1:2 molar ratios (host: guest) were prepared and formation of solid inclusion complexes was confirmed by means of FT-IR and \(^1\)H NMR spectroscopy. The results obtained confirmed the inclusion of PA into \(\beta\)-CD cavity. The significance of this work lies in the increase of PA bioavailability by complexation with \(\beta\)-CD and hence is a good pathway to make it potentially useful for its application as Anti-Fungal and Anti-microbial agent.

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Keywords: \(\beta\) - Cyclodextrin, Picric acid, FT-IR, \(^1\)H NMR and Inclusion Complexes

1. Introduction

There has been great interest for PA, an aromatic nitro compound in various fields like synthesis of a staining agent and as an antiseptic. PA (2, 4, 6-trinitrophenol) is a pale yellow, odorless crystalline solid that has been used as a military explosive, as a yellow dye and as an antiseptic. In homeopathy, it is used as a medicine for treating ‘burn out’ or exhaustion. PA is slightly soluble in water. In addition to its use in explosives, PA has been used in the synthesis of chloropiricin, or nitro trichloro methane (CCl\(_3\)NO\(_2\)), a powerful insecticide. It also acts as Anti-Fungal [1] and Anti-microbial [2] agents.

Cyclodextrins can increase the solubility of nitro phenolic compounds [3, 4]. Cyclodextrins form inclusion complexes, with different guest molecules having suitable polarity and dimensions [5, 6]. Cyclodextrins are cyclic oligosaccharides, which are connected at 1 and 4 carbon atoms. With six to eight \(\alpha\)-D-glucopyranose units they are called as \(\alpha\)-, \(\beta\)- and \(\gamma\)-Cyclodextrins respectively. The special characteristic of Cyclodextrins is the ability to form an inclusion complex having apolar nature [7]. The inclusion complex formation occurs through various interactions, such as hydrogen bonding, Van der Waals interaction, hydrophobic interactions and also electrostatic attraction. The physical, chemical and biochemical properties of guest molecules will be modified and their applications can be therefore enhanced [8].

PA forms crystalline picrates with various organic molecules through ionic, hydrogen bonding and \(\pi\)–\(\pi\) interactions [9]. Bonding involves not only electrostatic interactions but also formation of molecular complexes [10]. Taking into account the importance of aromatic nitro compounds herein we have prepared and studied inclusion complexes of PA with \(\beta\)-CD and confirmed the inclusion phenomenon by various physical measurements.

In this article, we focus on the interaction between \(\beta\)-CD and PA at different conditions. The results show that \(\beta\)-CD and PA form an inclusion complex, which increases the solubility of PA in water. The binding constant of the inclusion complex at different pH shows that the inclusion complex becomes unstable under alkaline condition and catalyzes its decomposition [11, 12]. The mode of inclusion of PA into \(\beta\)-CD cavity has been illustrated in Fig 1.