



Spectroscopic Characterization of Stability and Interaction of Pt-Sn Complexes with Different Capping Agents

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Abstract

Colloidal metal nanoparticles are of great interest because of their use as catalysts, photocatalyst, adsorbent and sensors and because of their application in optical, electronic and magnetic devices. Capping agents are widely used in the synthesis of colloidal nanocrystals, and their roles are generally as stabilizers. A heat-treatment method for the preparation of well-stable Pt-Sn complex is demonstrated using different capping agents such as mercaptosuccinic acid (MSA), mono ethylene glycol, polyacrylic acid, and poly (vinyl pyrrolidone) etc. The stability and interaction of Pt-Sn complexes with different capping agents were characterized by UV–via absorption spectroscopy. Pt-Sn bimetallic nanoparticles have been prepared and characterized by UV–via spectroscopy.

Keywords: Pt-Sn complexes; Capping agents; UV-spectroscopy; Stability

Introduction

Platinum, a precious transition metal that has outstanding catalytic and electrical properties and superior resistant characteristics to corrosion, has been widely applied in chemical, petrochemical, pharmaceutical, electronic, and automotive industries [1-4]. Supported bimetallic catalysts composed of platinum and tin loaded on alumina, silica, or carbon, have been widely studied for catalytic reactions such as dehydrogenation [5-8] and reforming reactions in petroleum or petrochemical industries. These bimetallic catalysts have generally shown enhanced catalytic stability and higher selectivity to the desired products compared to monometallic catalysts. The nature of supported bimetallics depends on the preparation methods including the sequence of metal loading, metal precursors, capping agent solvents, and the composition of two metals [5-16]. The positive effects of second metal addition to platinum catalyst have been generally explained in terms of electronic effects, geometric effects, or their combination through forming an alloy [6,7,14-16] or diluting platinum ensemble sites [5,8-13].

It is well understood that the properties of bimetallic nanoparticles for these applications are size and shape dependant [17-19].

New synthetic approaches for size- and shape-controlled nanoparticles synthesis using different ligands or capping agents are regularly investigated. In this realm the wet chemical synthesis of nanostructures is a very useful and versatile method.

Monometallic platinum particles have been prepared using various stabilizers including polymers, ligands, and surfactants. If classified according to the active atoms of the functional groups in the molecules, these stabilizers can be (a) oxygen containing, such as sodium citrate [20] poly (vinyl alcohol) [21] carbon monoxide [22] poly (ethylene glycol) monolaurate, and 10- undecenoic acid [23] nitrogen-containing (in some cases also containing oxygen), such as tetraalkylammonium [21,24] poly (vinyl pyrrolidone) (PVP) [21,25] poly (methyl acrylate-co-N-vinyl-2- pyrrolidone) [26] disodium 1,10-phenanthroline-4,7-bis (benzene- 4-sulfonate), [27] poly(N-isopropylacrylamide), [28] and p-aminobenzenesulfonate; [29] phosphorus-containing, such as polyphosphate [30] and phosphine [31,32].

Sulfur-containing molecules such as thiolates using substituted thioacids have rarely been used directly for the synthesis of Pt nanoparticles.

Polymers and glycols like mono ethylene glycol are widely used

in the chemical synthesis of colloidal nanocrystals, and their roles are generally documented as steric stabilizers or capping agents [33-40]. In particular, poly (vinyl pyrrolidone) (PVP) and polyacrylic acid (PAA) has received special attention because of its high chemical stability, nontoxicity, and excellent solubility in many polar solvents [33,34]. Like long-chain alcohols, we suspect that such polymers can serve as a new class of reductants, whose mild reducing power is desired for kinetically controlled synthesis of metal nanocrystals [35,36].

The present papers gives detailed account of experiments carried out in laboratory to study the stability and formation of Pt-Sn bimetallic nanoparticles using various capping agents.

Experimental Section

Chemicals

Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) was purchased from M/s Parekh Platinum Pvt. Ltd. Mumbai, India. Tin chloride hydrate was purchased from Merck India Pvt. Ltd. Mumbai, India. Ethylene Glycol, Polyacrylic acid, Poly (vinylpyrrolidone) (PVP, MW=40000) and conc. hydrochloric acid was purchased from CHITI-CHEM Corporation, Baroda, India. All the chemical used of analytical grade and were used without any further purification.

Preparation of platinum-tin complex

Preparation of Pt-Sn complex without capping agent: 0.19 wt% Pt (0.7325 gm of chloroplatinic acid), 0.21 wt% Sn (0.42 gm of tin chloride, hydrate), and 2 wt% hydrochloric acid (0.58 gm of conc. HCl) mixed together. A dark red colored Pt-Sn complex formed and further make up to 100 ml volumetric flask (1:10 water: conc. HCl). Again 5 ml solution from 100ml stock solution taken and make up to 25 ml

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(1:10 water: conc. HCl) which is used analysis. The Pt-Sn complexes obtained were characterized by light absorption spectra using Perkin-Elmer Lambda 35 UV/Vis spectrometer at different interval of time has been measured. Water was used as the reference solution. The image of Pt-Sn complex solution without any capping agent which is dark red color (Figure 1a).

Preparation of Pt-Sn Complex with different capping agent: 0.19 wt% Pt (0.7325 gm of chloroplatinic acid), 0.21 wt% Sn (0.42 gm of tin chloride, hydrate), 2 wt% hydrochloric acid (0.58 gm of conc. HCl) and appropriate quantity of capping agent mixed together and heat for 15 min at 60-70°C. The bright red colored Pt-Sn complex solution turns light yellow after addition of capping agent specially mercaptosuccinic acid and this effect was not observed any other capping agents. The complex solution cooled down and make up to 100 ml volumetric flask (1:10 water: conc. HCl). Again 5 ml solution taken from 100 ml stock solution and make up to 25 ml (1:10 water: conc. HCl). The same solution is directly used for UV analysis and absorbance at different interval of time has been measured. The similar method is used for all capping agents to measure UV absorbance. The image of Pt-Sn complex after addition of mercaptosuccinic acid as a capping agent (Figure 1b).

The above prepared Pt-Sn complex solution bubbled with hydrogen gas in order to reduce the metals to form Pt-Sn bimetallic nanoparticles. These nanoparticles formation was confirmed by UV analysis.

The general schematic diagram for Pt-Sn complex preparation and nanoparticles formation (Figure 2).

Results and Discussions

The stability of Pt-Sn complexes with various capping agents such as mercaptosuccinic acid (MSA), mono ethylene glycol, poly (vinyl pyrrolidene) and polyacrylic acid (PAA) are studied in detail by using Ultra-Violet spectroscopy.

UV-vis spectra of the Pt-Sn complex

When the solution of tin chloride hydrate (0.42 gm) and 2 wt% conc. hydrochloric acid (0.58 gm) was added to chloroplatinic acid hexahydrate solution, the solution transformed to a dark red clear solution, indicating the formation of some complex ions due to transfer of electrons. Rodriguez et al. reported that $[PtCl_2(SnCl_3)_2]^{2-}$ complex



Figure 1a: Image of Pt-Sn complex solution.

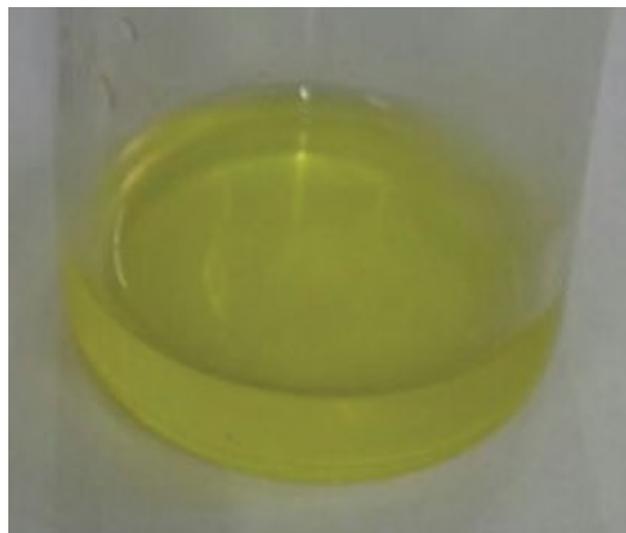
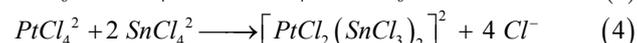
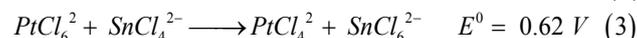
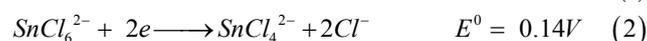
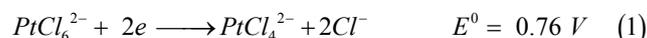


Figure 1b: Image of Pt-Sn complex solution after capping agent addition.

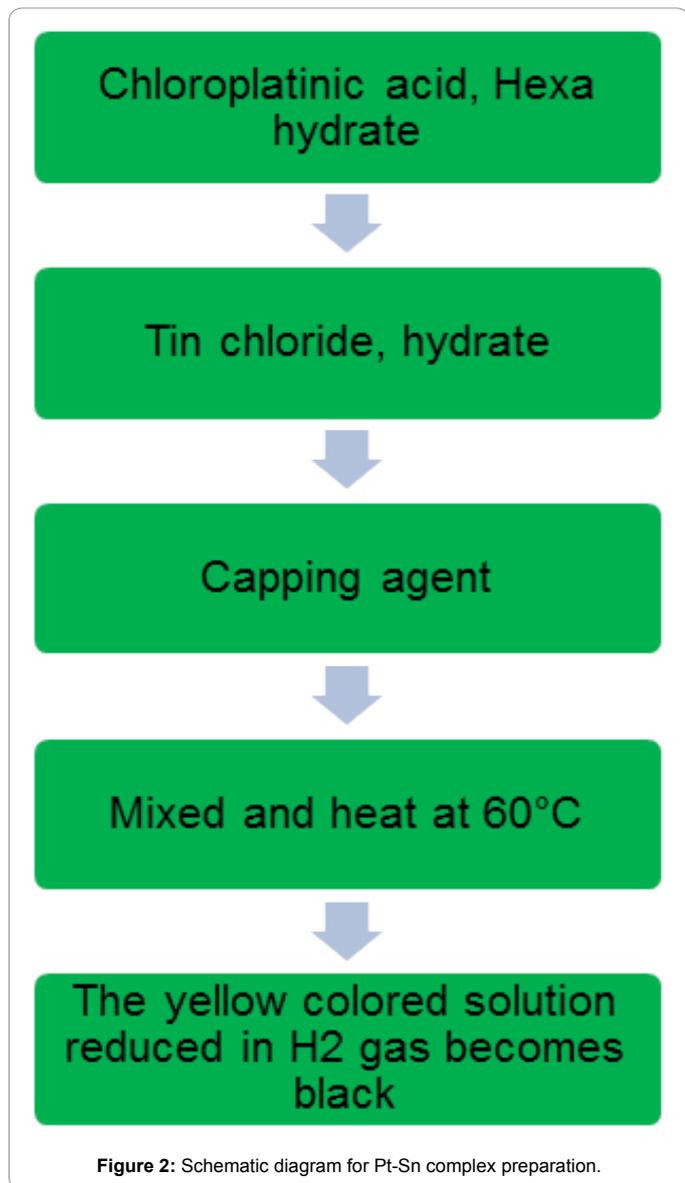
ions can be formed, when chloroplatinic acid hexahydrate mixed with tin chloride in the presence of acid media [39,40]. The fresh dark red complex solution used for UV analysis. It is observed from Figure 3 also reported by Baronett et al. that there is a prominent absorption peak at around 262 nm for H_2PtCl_6 and no absorption peak for $SnCl_2$. The absorption peak at 262 nm can be assigned to Pt (IV). However, when the $[PtCl_2(SnCl_3)_2]^{2-}$ complex ions were formed, the absorption peak at 265 nm reduced and there appeared novel peaks at 276, 365, 417, and 488 nm. These bands can be assigned to the $[PtCl_2(SnCl_3)_2]^{2-}$ complex being related the Sn (IV) species (276 nm), to the charge transfer of the ligands $[SnCl_3]^-$ to platinum (365 nm) and to d-d transitions (417 and 488 nm).

So it could be deduced that Pt (IV) ions were reduced to form Pt (II) ions by Sn (II) ions, and then Pt (II) ions reacted with Sn (II) ions to form the multi-nuclear complex ions $[PtCl_2(SnCl_3)_2]^{2-}$. When the $[PtCl_2(SnCl_3)_2]^{2-}$ complex ions were reduced, all the absorption peaks disappeared, indicating that the Pt-Sn bimetallic nanoparticles were formed for that Pt and Sn nanoparticles have no absorption peak in this range. The possible reaction pathways during Pt-Sn complex formation as per literature reports are mentioned below:



In order to study the stability of Pt-Sn complex with respect time, the absorption spectra recorded after 1, 2, 3 and 4 hrs. From Figure 4, it is observed that with respect to time, the stability of the complex decreases and also observed that the color changes from dark red to colorless after 4 hours. So we decided to prepare all fresh Pt-Sn complex solution for UV analysis.

In order to study the stability of Pt-Sn complex, we also increased the weight percentage of hydrochloric acid up to 5 and 10 wt% and recorded the absorption spectra at different time interval. From Figures 5a and 5b it is observed that with increase in hydrochloric acid concentration, there is no effect on Pt-Sn complex stability. So the



optimum 2 wt% hydrochloric acid concentration is used to prepare all Pt-Sn complexes with different capping agent.

UV-vis spectra of the Pt-Sn complex with (MSA)

0.19 wt% Pt (0.7325 gm of chloroplatinic acid), 0.21 wt% Sn (0.42 gm of tin chloride, hydrate), 2 wt% hydrochloric acid (0.58 gm of conc. HCl) and 0.05 gm 0.05 wt% mercaptosuccinic acid (0.05 gm MSA) mixed together and heat for 15 minutes at 60-70°C. The yellow color Pt-Sn complex mixture is formed, and cooled down for further analysis. The fresh solution is directly used for UV analysis and an absorbance spectrum was recorded.

From Figure 6, it is clear that Pt-Sn complex using mercaptosuccinic acid as capping agent did not show any specific absorption peak, there is slight small peak at 294 nm. It means that under the treatment with mercaptosuccinic acid, Pt-Sn complex may not be stable.

UV-vis Spectra of the Pt-Sn complex with monoethylene glycol (MEG)

0.19 wt% Pt (0.7325 gm of chloroplatinic acid), 0.21 wt% Sn (0.42

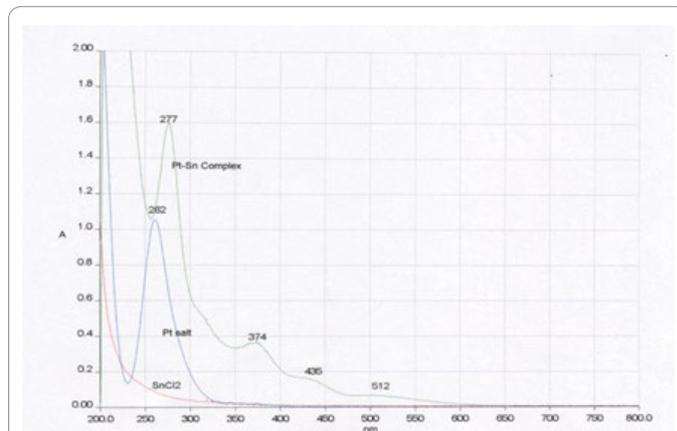


Figure 3: UV spectra of chloroplatinic acid, tin chloride and Pt-Sn complex.

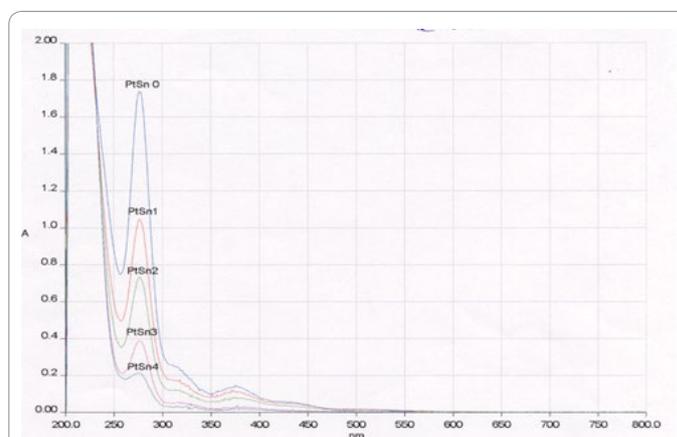


Figure 4: Stability Pt-Sn complex at different time intervals.

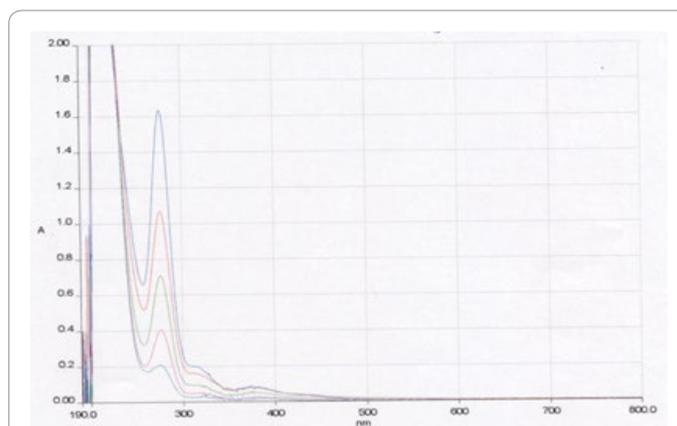
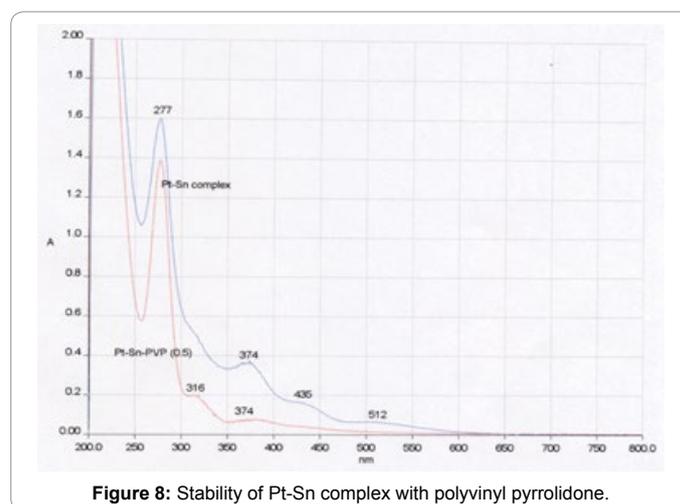
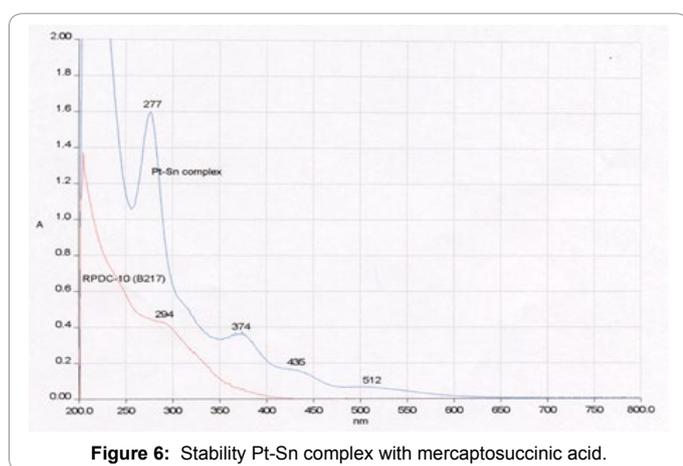
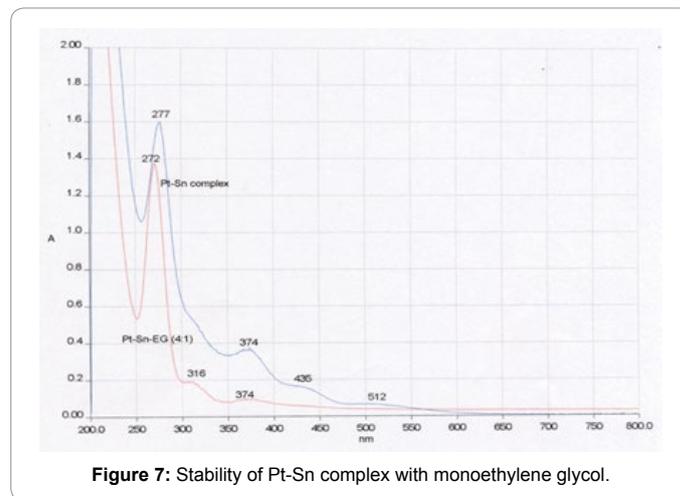
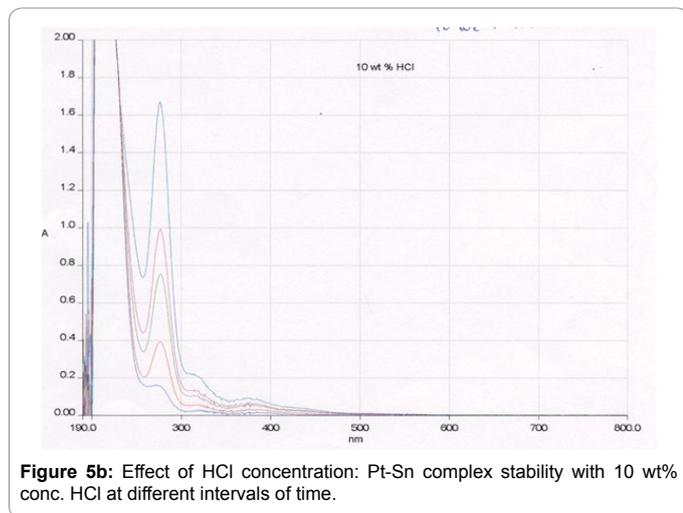


Figure 5a: Effect of HCl concentration: Pt-Sn complex stability with 5 wt% conc. HCl at different interval of time.

gm of tin chloride, hydrate), 2 wt% hydrochloric acid (0.58 gm of conc. HCl) and 0.05 gm 0.025 wt% monoethylene glycol (0.025 gm MEG) mixed together and heat for 15 min at 60-700°C. The bright red color Pt-Sn complex mixture is formed and cooled down. The fresh same solution is directly used for UV analysis and absorbance spectra were recorded.

From Figure 7, it is observed that Pt-Sn complex with monoethylene



glycol (MEG) shows one novel absorption peak at 316 nm with disappearance of 435 and 512 nm observed in Pt-Sn complex without any capping agent. It indicates that due interaction of Pt-Sn with MEG there is upward shift in absorbance but the Pt-Sn complex is stable as observed in case of mercaptosuccinic acid.

UV-vis spectra of the Pt-Sn complex with polyvinyl pyrrolidone

0.19 wt% Pt (0.7325 gm of chloroplatinic acid), 0.21 wt% Sn (0.42 gm of tin chloride, hydrate), 2 wt% hydrochloric acid (0.58 gm of conc. HCl) and 0.05 gm 0.005 wt% poly (vinyl pyrrolidone) (0.005 gm PVP) mixed together and heat for 15 min at 60-700°C. The bright red color Pt-Sn complex mixture is formed and cooled down. The fresh solution is directly used for UV analysis and absorbance spectra were recorded.

From Figure 8, it is observed that Pt-Sn complex with PVP shows similar absorption pattern like Pt-Sn with mono ethylene glycol. It indicates that the due interaction of Pt-Sn with PVP the complex is stable.

UV-vis Spectra of the Pt-Sn complex with poly acrylic acid (PAA)

0.19 wt% Pt (0.7325 gm of chloroplatinic acid), 0.21 wt% Sn (0.42 gm of tin chloride, hydrate), 2 wt% HCl (0.58 gm of conc. HCl) and 0.0625 wt% poly acrylic acid (0.625 gm PAA) mixed together and heat for 15 min at 60-70°C. The bright red color Pt-Sn complex is formed and cooled. The fresh same solution is directly used for UV analysis and absorbance spectra were recorded.

From Figure 9, it is observed that in case of PAA as capping agent, Pt-Sn complex with PAA shows similar absorption pattern at 276, 365, 417, and 488 nm like Pt-Sn complex without any capping agent. It indicates that Pt-Sn complex is stable using PAA as ligand.

When the above Pt-Sn complex solution PAA bubbled with hydrogen gas for 15 minute at room temperature. $[PtCl_2(SnCl_3)_2]^{2-}$ complex ions were reduced and all the absorption peaks at 276, 365, 417, and 488 nm disappeared as shown in Figure 10. The color of the complex solution gradually changed from dark red to full dark indicating that the Pt-Sn bimetallic nanoparticles were formed for that Pt and Sn nanoparticles have no absorption peak in this range.

Conclusion

Pt-Sn complexes have been prepared by using different capping agents like mercaptosuccinic acid (MSA), mono ethylene glycol (MEG), poly (N-vinyl-2-pyrrolidone) (PVP), and polyacrylic acid (PAA). The stability of Pt-Sn complexes with various capping agents were studied by ultra-violet visible spectroscopy. Pt-Sn bimetallic nanoparticles were prepared and characterized by UV spectroscopy. The concept of Pt-Sn complex formation and stability with various ligands/capping agents can be used in the preparation supported bimetallic catalyst for dehydrogenation reactions to increase the metal dispersion as well as stability of the catalyst.

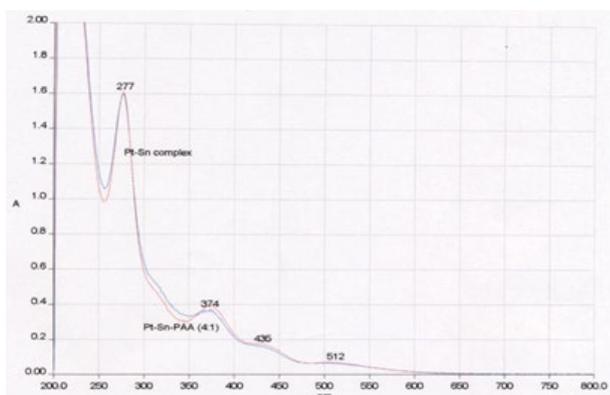


Figure 9: Stability of Pt-Sn complex with polyacrylic acid.

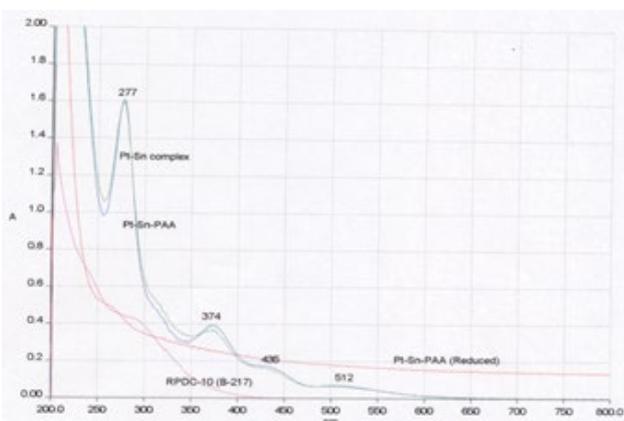


Figure 10: Stability of Pt-Sn complex with PAA reduced with H₂ bubble.

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