

SYNTHESIS AND CHARACTERIZATION OF POLY DEOXYCHOLIC ACID ENCAPSULATED COPPER NANOPARTICLES AND ITS CATALYTIC APPLICATION

S. SENGUTTUVAN

Department of Chemistry, Vel Tech (owned by R.S.Trust) Avadi, Chennai-600062, (India)

T. HEMALATHA

Department of Chemistry, Srivengateswara Engineering College of Engineering and Technology, Tirupachu, Thiruvallur-631203 (India)

A. YOGANANTH

Department of Chemistry, Vel Tech Multi Tech Engineering College, Avadi, Chennai-600062 (India)

AND

R. VARUN STANLEY

Department of Physics, Aarupadai Veedu Institute of Technology, Kancheepuram-603104 (India)

RECEIVED : 8 January, 2014

The poly (deoxycholic acid) encapsulated copper nanoparticle has been synthesized through condensation polymerization at ambient temperature by using NaBH_4 as reducing agent and ascorbic acid as surface productive agent at basic pH. The rate of the nanoparticle formation will be optimized by varying the concentration of polymer and metal salt. The dye formation depends on the pH, nature of 4 -AAP and the medium. Characterization of newly synthesized copper nanoparticles was analyzed by using UV- vis spectroscopy. FT-IR spectra of the dye formed between aniline and 4-AAP in the presence of copper catalyst was recorded in KBr. The mechanism has been proposed with the help of its kinetics effects. The size of the nanoparticles has been confirmed by TEM analysis.

INTRODUCTION

In this context, oxidative coupling reactions of amines in the presence of chromogenic electron donor species provide a way to have a simple quantitative photometric assay to determine the formation of the reaction product. So that adequate processes can be developed and implemented, there is a fundamental need to understand the kinetics of the system, as this is essential for process design and optimization of the operation [1-8]. In earlier studies, the reaction between aniline and phenol with 4-AAP in the presence of H_2O_2 catalyzed by tetrasulfophthalocyanine was found to produce an intense pink and red-colored water-soluble dye product that is precisely and easily detected and estimated using UV-Vis spectroscopy [9, 10]. In continuation of our earlier work, we now report a dye formation reaction between 4-AAP and aniline derivatives in the presence of copper nanoparticles as a catalyst without the addition of H_2O_2 as an oxidant. The dye formation reaction does not proceed without a catalyst [11]. However, the addition of copper nanoparticles into the reaction mixture containing aniline derivatives with 4-AAP causes the formation of characteristic colors of the respective antipyrilquinoneimine dye. The kinetics of the dye formation can be monitored by UV-Vis

spectroscopy at various time intervals at the characteristic λ_{max} of the corresponding dye. The catalytic activity of copper nanoparticles in aqueous medium is of great interest due to its greater stability, higher number of active sites on the surfaces of smaller particles, leading to higher rate constants for many reactions [12-15]. In this study, the maximum rate constant of the reaction is optimized by investigating the effects of various compositions of aniline derivatives, 4-AAP, copper nanoparticles, pH and temperature of the reaction medium. We further calculate the rate constants and activation energies from the resultant slope values. We clarify the interactions of aniline derivatives with 4-AAP using these kinetic parameters, and analyze the role of copper nanoparticles in the reaction pathway.

EXPERIMENTAL

The copper nanoparticles are synthesized and characterized. UV-visible spectra were recorded on Shimadzu UV-1601 spectrophotometer. The FT-IR spectra were recorded using Perkin-Elmer FT-IR spectrophotometer.

Synthesis of Copper Nanoparticles in Aqueous Medium

The metal nano colloids were prepared in a four-necked round bottom flask following the reported procedure with small modifications [16-17]. All solutions were prepared using deionised water double distilled water. The four-step preparation scheme for copper nanoparticles starts with dissolving copper (II) sulfate pentahydrate salt, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.01 M), in deionized water to obtain a blue solution. Next, poly deoxycholic acid (0.0018 g in DMF: H_2O ratio of 1:49) was dissolved in water and added to the aqueous solution containing the copper salt while vigorously stirring. In this step, the solution changed from blue to white. In the third step, ascorbic acid (0.02 M) and sodium hydroxide (0.1 M) were dissolved in water and added to the synthesis solution. Colour change occurred in the aqueous phase from white to yellow. Finally, a solution of NaBH_4 (0.1 M) in deionized water was prepared and added to the solution under continuous rapid stirring. An instant color change occurred in the aqueous phase from yellow to red [16]. The appearance of this dark color indicated that the reduction reaction had started. The source of electrons for the reaction was BH_4^- . The mixture was further stirred rapidly for around 10 min in ambient atmosphere, to allow the reaction to complete.

Kinetic Measurements

All reactions were carried out with fresh solutions. The initiation of the reaction was considered as the time of addition of copper nanoparticles into the reaction mixture containing the aniline derivative and 4-AAP. Kinetic plots of $\log X$ versus time were constructed, where $X = [(\text{OD}_\infty)/(\text{OD}_\infty - \text{OD}_t)]$ and OD_t and OD_∞ refers to absorbance at time t and at completion of the reaction respectively. The plots were used to determine the rate coefficient values. The kinetic plots were used to determine the rate constant values by maintaining 4-AAP concentration nearly 10 times greater than the amine concentration in accordance with pseudo first order conditions.

RESULTS AND DISCUSSION

Effect of Substituent on Aniline Derivatives

The UV-Vis stacked spectra of the dye formation reaction between 4-AAP and poly (deoxycholic acid) in the presence of the copper nanoparticles catalyst at different time intervals. The rate of reaction increases with increasing the concentration of aniline. Which are

conformed from the extent of increasing the absorption peak intensity at 330 and 520 nm. The resultant absorption changes at various time intervals for different concentration of aniline with 4-AAP in presence of catalyst are shown in Fig. 1(a). The kinetic plot can be obtained from the absorption versus time measurement at various concentration of 4-AAP. An increasing the concentration of 4-AAP the rate values increases which are revealed in the greater the slope values are shown in Fig.1(b) and the corresponding rate values are given in table 1.

Table 1: Rate constants values of antipyrilquinoneimine coupling product formation using various concentration of 4-AAP, Aniline in presence of 1×10^{-4} M of CuNPs.

[4-AAP] M	Rate $k \times 10^2$ (s ⁻¹)	[Aniline] M	Rate $k \times 10^2$ (s ⁻¹)
0.001	0.97	0.0001	1.66
0.003	1.53	0.0003	2.45
0.005	2.04	0.0005	2.58

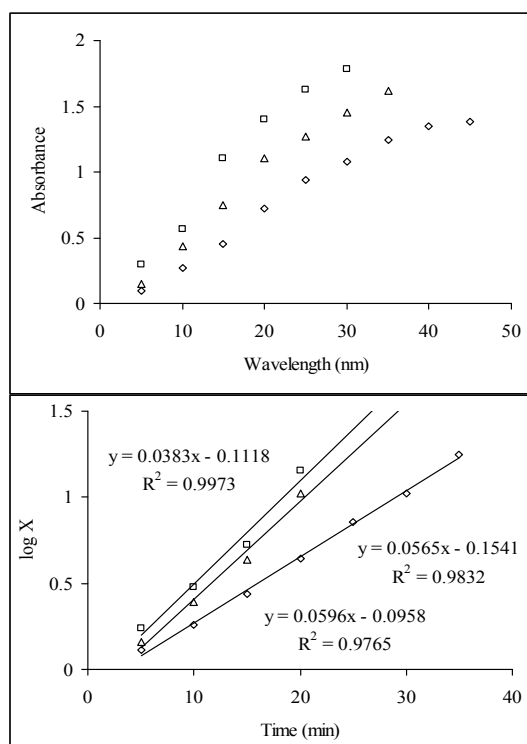


Fig. 1. Absorbance versus time plots (a) and kinetic plots (b) of antipyrilquinoneimine dye formation between various concentration of aniline and 4-AAP (0.003M) in presence of copper catalyst. (\diamond) 1×10^{-4} M, (Δ) 3×10^{-4} M and (\square) 5×10^{-4} M.

Effect of 4-AAP concentration

UV-visible stacked spectra of different concentration of 4-AAP with aniline in presence of copper nanoparticles at various time intervals. The initiation of the reaction is considered at the time of addition of copper nanoparticles into the reaction mixture. As the reaction proceeds the light yellow colour of the solution turns to pink colour. The decreasing the intensity of the peak at 280 nm confirms the consumption of 4-AAP in the reaction. However, the appearances of new peaks at 335nm and 540 nm is conforms the antipyrilquinoneimine dye formation. The optical density versus time dependant plot at constant composition of catalyst and aniline in presence of different the concentration of 4-AAP are shown in Fig 2.

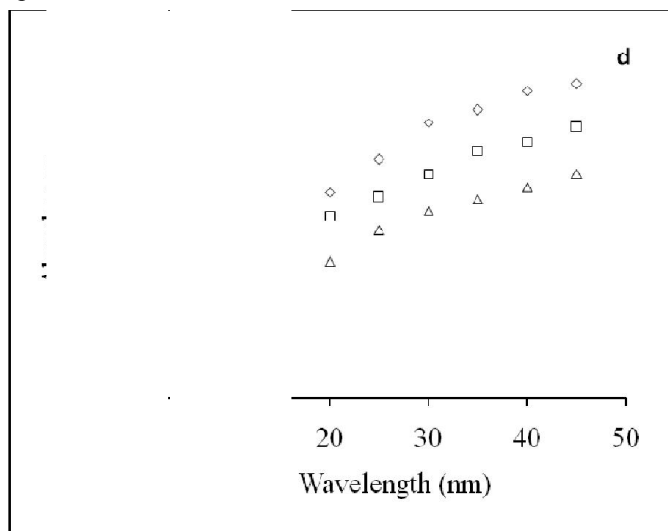


Fig. 2. Optical density versus time dependent plots of antipyrilquinoneimine dye formation between various concentration of 4-AAP and aniline 1×10^{-4} M in presence of copper catalyst at 25°C.

Effect of pH on the dye formation reaction

The pH of the reaction was also found to have a significant role in the dye formation reaction. The typical UV-visible spectra of antipyrilquinoneimine dye formation at constant composition of copper nanoparticles (1×10^{-4} M), aniline (3×10^{-4} M) and 4-AAP (0.003M) in presence of various pH such as 3.2; 5.6; 8.2; and 9.2 as shown in Fig. 3.

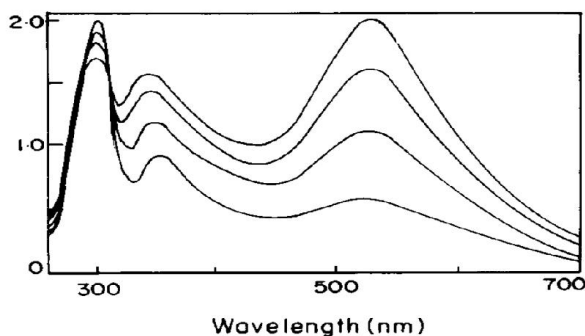


Fig. 3. UV-visible spectra of on the dye formation reaction between aniline and 4-AAP in presence catalyst at different pH in aqueous medium.

From this spectra we observed that in acidic pH, the intensity of absorbance values are low due to existence of protonated form of amine groups. It increases significantly when pH is raised and the maximum rate constant is attained at pH 9.0 (listed in Table). This may be due to the pK_b value of aniline group, which falls at 9.4. Hence, the electron donor capacity of amine react effectively with 4-AAP to form stable antipyrilquinoneimine which are reflected in the high intensity optical density values. Therefore rate of dye formation with respect to pH variation falls in the following order $9.2 > 8.2 > 5.6 > 3.2$.

Characterisation studies

UV-Visible absorption spectra have been proven to be quite sensitive to the formation of copper nanoparticles. An intense absorption band at 565 nm was generally observed for copper nanoparticles [17] and attributed to the surface plasma on excitation of Cu particles as shown in Fig. 4. In a typical reaction, dilute copper (II) solution was dissolved into aqueous poly deoxycholic acid (3 ml) and then the mixture was poured into dilute freshly prepared sodium borohydride solution and the final volume was adjusted with water at room temperature. The mixture turned first yellow, then orange and finally red. The appearance of a reddish color indicated the presence of copper nanoparticles.

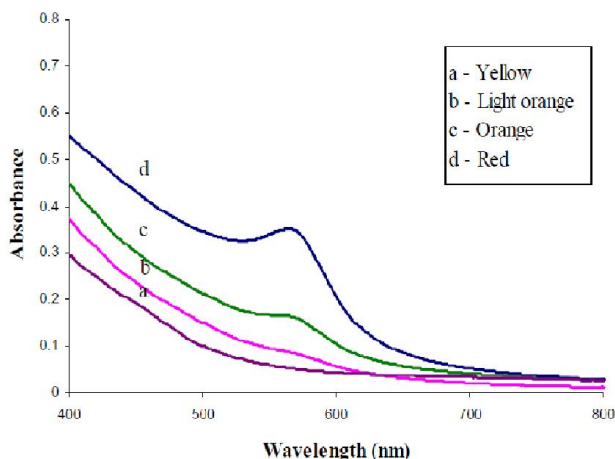


Fig. 4. Stacked UV-visible spectra of poly (deoxycholic acid) stabilized copper nanoparticles using 0.005 M of CuSO_4 ions and 0.05M of NaBH_4 at room temperature in aqueous medium.

The plasmon absorbance near 560 nm was present in a spectrum taken within minutes after the color appeared (Figure 4).

Transmission electron microscopy has provided further insight into the morphology and size details of the copper nanoparticles. A representative TEM image recorded from the copper nanoparticles solution is shown in Fig. 5. The poly (deoxycholic acid) stabilized copper nanoparticles was prepared using NaBH_4 as reducing agent in aqueous medium. It has been confirmed that the copper nanoparticles mostly exist in the spherical and few rod shape structure. The average size of the nanoparticles was found to be 16 nm.

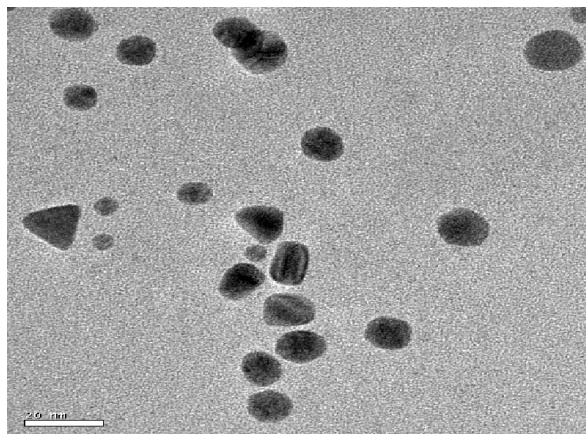


Fig. 5. Transmission electron microphotograph of poly (deoxycholic acid) capped copper nanoparticles in aqueous medium, on formvar coated copper grids.

Mechanism of dye formation

The mechanism has been proposed on the basis of result obtained from UV-visible and FT-IR measurements. Copper catalyse the dye reaction between 4-AAP and aniline are conducted at different experimental conditions. This reaction does not proceed in the absence of nanoparticles. When catalyst is added to substrates and 4-AAP mixed solutions the intensity of absorbance at 330 and 520 nm increases which confirms the antipyrilquinoneimine. FT-IR spectra of antipyrilquinoneimine dye shows the interaction mode of functional group of 4-AAP with aniline. The band appeared at 1600 cm^{-1} corresponds to C=O vibration and the band at 3300 cm^{-1} corresponds to N-H group vibration as shown in Fig. 4.6. Therefore, based on the experimental data the proposed reaction is given in the following Scheme I.

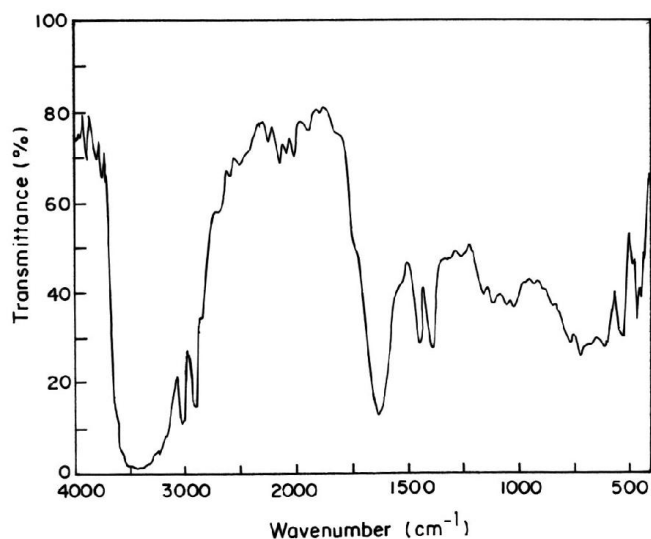
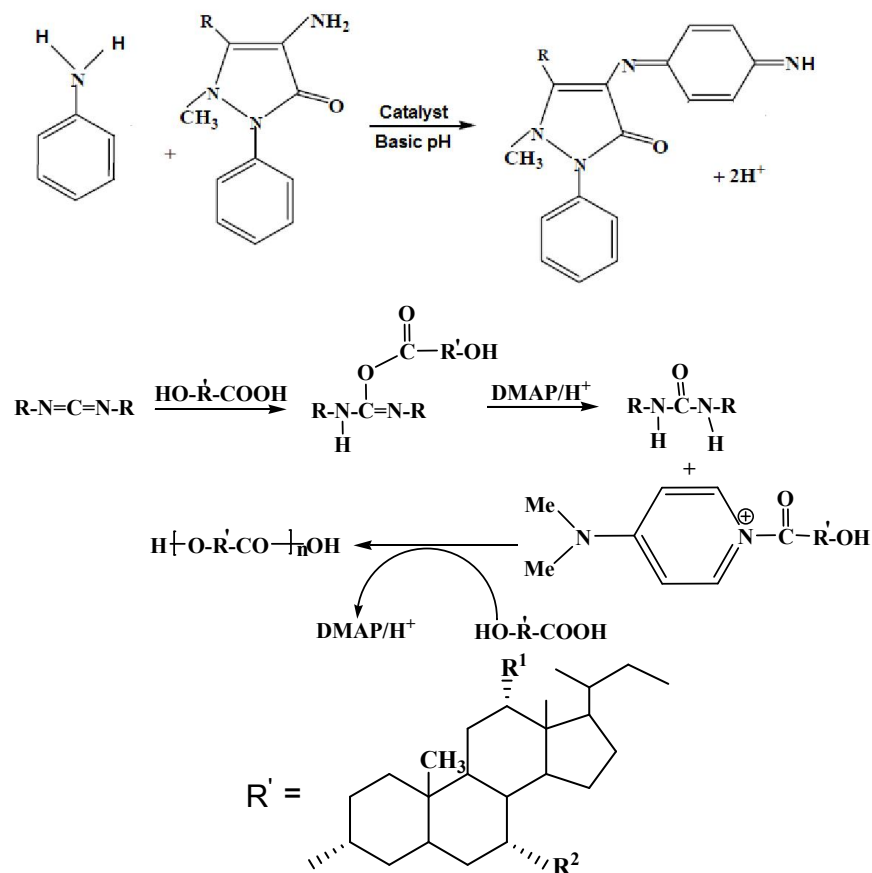


Fig. 4.6. FT-IR spectra of antipyrilquinoneimine dye

Scheme 1. Reaction mechanism of poly(deoxycholic acid) obtained by polycondensation of deoxycholic acid



CONCLUSIONS

The studied dye formation reaction between substituted anilines and 4-AAP catalyzed by copper nanoparticles revealed pseudo first order kinetics with respect to each reactant. Regarding the study of the variables of substrates, pH, salt and temperature, the reaction does not proceed in the absence of the catalyst nor at basic pH. The observed rate constants for anilines with electron donating groups are greater than those with electron withdrawing groups. At acidic pH values, the rate constant of the reaction increases to a maximum rate at pH 9.2. The activation energy of aniline derivatives with electron donating groups is lower than those with electron withdrawing groups. The report illustrates a novel spectrophotometric technique for the detection of aromatic amines in aqueous solutions *via* coupling reaction.

REFERENCES

1. Debruin, L.S., Pawliszyn, J.B., Josephy, P.D., *Chem. Res. Toxicol.*, **12**, 78 (1999).
2. Mishra, S., Singh, V., Jain, A., Verma, K.K., *Analyst*, **126**, 1663 (2001).
3. Clark, E.A., Anliker, R., Hutzinger, O., *The Handbook of Environmental Chemistry Berlin: Springer-Verlag*, **3A**, 181 (1980).
4. Villalobos, D.A., Buchanan, I.D., *J. Environ. Eng. Sci.*, **1**, 65 (2002).

5. Oyama, M., Kirihara, K., *Electrochimica. Acta*, **49**, 3801 (2004).
6. Kadar, M., Nagy, Z., Karancsi, T., Farsang, G., *Electrochimica. Acta*, **46**, 1297 (2001).
7. Pramauro, E., Prevot, A.B., Augugliaro, V., Palmisano, L., *Analyst*, **120**, 237 (1995).
8. Seymour, E.H., Lawrence, N.S., Beckett, E.L., Davis, J., Compton, R.G., *Talanta*, **57**, 233 (2002).
9. Brillas, E., Mur, E., Sauleda, R., Sanchez, L., Peral, J., Domenech, X., Casado, J., *Appl. Catal. B: Environ.*, **16**, 31 (1998).
10. Rajendiran, N., Santhanalakshmi, J., *J. Mol. Catal. A: Chem.*, **245**, 185 (2006).
11. Degrand, C., Limoges, B., Martre, A.M., Schollhorn, B., *Analyst*, **126**, 887 (2001).
12. Yu, W.W., Liu, H., *J. Mol. Catal. A: Chem.*, **243**, 120 (2006).
13. Cerro-Alarcon, M., Maroto-Valiente, A., Rodriguez-Ramos, I., Guerrero-Ruiz, A., *Carbon*, **43**, 2711 (2005).
14. Spitaleri, A., Pertici, P., Scalera, N., Vitulli, G., Hoang, M., Turney, T.W., Gleria, M., *Inorganica. Chimica. Acta*, **352**, 61 (2003).
15. Roucoux, A., Schulz, J., Patin, H., *Chem. Rev.*, **102**, 3757 (2002).
16. Brillas, E., Mur, E., Sauleda, R., Sanchez, L., Peral, J., Domenech, X., Casado, J., *Appl. Catal. B: Environ.*, **16**, 31 (1998).
17. Dang, Thi My Dung, Le, Thi Tuyet Thu, Fribourg-Blanc, Eric and Dang, Mau Chien, *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, **2**, 015009 (2011).

