



Silver Nanoparticles-Based Nano-drop Spectrophotometric Determination of Cationic Surfactants Coupled with Hydrophobic Interaction; An Application to Pharmaceuticals and Environmental Samples

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ABSTRACT

The proposed work describes the nanodrop spectrophotometric determination of cationic surfactants using citrate-modified silver nanoparticles based on the aggregation of silver nanoparticles induced by cationic surfactants due to the hydrophobic effect. The visible color change in the solution of silver nanoparticle includes a red shift with the quenching of the absorption spectra. The maximum absorbance was measured at wavelength, λ_{max} 400 nm. The concentrations of cationic surfactants were determined using a nanodrop spectrophotometer with limits of detection of 15.0, 8.0, 6.0, 5.8, and 13.0 μ M for dodecyl trimethyl ammonium bromide, myristil trimethyl ammonium bromide, cetrimonium trimethyl ammonium bromide, cetyl pyridinium chloride and benzalkonium chloride, respectively. The proposed method was successfully applied for the determination of cetyl pyridinium chloride in commercial mouthwisher, gum astringent and nasal spray pharmaceuticals and environmental samples.

Keywords: Silver nanoparticles; Aggregation; Cationic surfactants; Hydrophobic effect; Pharmaceutical; Environmental sample.

INTRODUCTION

Surfactants are surface-active compounds that can reduce the surface tension of water when used in very low concentrations. Surfactants are amphiphilic compounds. One end of the surfactant is hydrophilic (water soluble), and the other end is hydrophobic (water insoluble)¹. The hydrophobic ends are generally natural fats and oils. The

hydrophilic ends may be cationic, anionic and nonionic in nature. The most commonly used cationic surfactant is cetrimide, which contains tetradecyl trimethyl ammonium bromide with a minimum amount of dodecyl and hexadecyl compounds². Anionic surfactants include carboxylates (soaps), sulfates, and sulfonates. Cationic surfactants (CSs) are widely used in various pharmaceutical, cosmetic and industrial applications. CSs are the

main component of disinfectant fluid and act as biocides, emulsifiers, and wetting agents. Allergic reactions and inflammation can be caused by CSs in some sensitive persons; in particular, they can cause corneal damage when exposed to the eye³. CSs have become pollutants as a result of their deposition on land or into water bodies, and many are toxic to aquatic organisms⁴. Therefore, determination of quaternary cationic surfactants such as dodecyl trimethyl ammonium bromide (DTAB), myristil trimethyl ammonium bromide (TTAB), cetrimonium trimethyl ammonium bromide (CTAB), cetyl pyridinium chloride (CPC) and benzalkonium chloride (BZK) is very important.

There are several techniques for the determination of CSs, including capillary electrophoresis (CE)⁵, two-phase titration⁶, reversed-phase high-performance liquid chromatography (RP-HPLC)^{7,8}, gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS)⁹, UV visible spectrophotometry¹⁰⁻¹² and Rayleigh light scattering (RLS)¹³. These techniques are costly, consume a large amount of time and chemicals, require complicated operating steps and are inconvenient for outdoor detection. Therefore, we need to develop simple, rapid and sensitive methods for the determination of quaternary ammonium surfactants. The newest procedure, nanodrop spectrophotometric (NDS) determination, was applied to the determination of cationic surfactants based on a color change originating from the interaction of CSs and silver nanoparticles (Ag NPs), which is a fast, cost-beneficial procedure that is less time consuming. NDS avoids the use of large volumes of reagent solution; 1.0 μ L of sample solution is sufficient for the spectrophotometric measurements (<http://www.nanodrop.com/library/nd-1000-v3.7-users-manual-8.5x11.pdf>). The proposed method is simple, rapid and low cost, and it is more applicable for on-site determinations.

In previously reported methods, various reagents, such as orange (II), tetra bromo phenolphthalein ethyl ester, bromophenol blue, quinidine and pyrocatechol violet, have been used for the spectrophotometric determination of CSs¹⁴⁻¹⁸. However, due to interference of some common ions, these reagents cannot be used. The Fe (III)-SCN⁻ method was used for CSs determination,

but interference of the reducing and oxidizing agents was observed¹⁹. The bismuth (III) iodide method²⁰ was also used for CS determination.

Noble metal nanomaterials (e.g., Au and Ag) have been commonly used to develop highly sensitive colorimetric probes for the determination of biomolecules^{21,22}, drugs²³, toxicants²⁴⁻²⁸ and small molecules²⁹⁻³¹ due to their optical and electrical properties and biocompatibility^{32,33}. Ag nano materials are more cost effective in their preparation than Au nano materials.

In the proposed work, we demonstrated a novel concept of CS determination by developing an Ag NP-based colorimetric system. The aggregation of Ag NPs with the addition of CSs due to hydrophobic effects results in color change, which is visible. The strategy is shown in scheme 1. The development of the CS determination method was successfully applied for the analysis of our model CS, CPC in pharmaceuticals and environmental samples.

MATERIALS AND METHODS

Instrumentation

A nanodrop spectrophotometer (NDS, Model No.1000, Thermo Scientific Inc., Wilmington, Delaware, USA) with a path length of 1.0 mm was used for the absorbance measurements. An HR-TEM JEM-2100, JOEL (Philips, JAPAN) was used for the particle size analysis. Fourier transform infrared (FTIR) spectroscopy was performed on a Thermo Nicolet, Avatar 370 model with the spectral range 4000-400 cm^{-1} (Thermo scientific, USA) for the structural characterization of the NPs and the study of their size morphology. An LI-617 pH meter (Elico, Hyderabad, India) was used for pH measurements, and a Spinot magnetic stirrer with hot plate (Singhla Scientific Industry, Ambala Cant, India) was used for the Ag NPs preparation.

Chemicals and reagents

Silver nitrate (AgNO_3 , 99.8%) and conc. HCl (38%) were purchased from Qualigen, Fischer Scientific, Mumbai, India. Sodium chloride (99.5%) was obtained from OCPW, Calcutta, India. Sodium hydroxide (99.5%) and trisodium citrate ($\geq 98.0\%$) were obtained from Merck, Mumbai, India. Dodecyl trimethyl ammonium bromide (DTAB, $\geq 95.0\%$),

myristil trimethyl ammonium bromide (TTAB, $\geq 99.0\%$) and benzalkonium chloride (BZK, $\geq 95.0\%$) were obtained from Sigma Aldrich, St. Louis, USA. Cetrimonium bromide (CTAB, 98.0%) and cetyl pyridinium chloride (CPC, 99.0%) were purchased from LOBA Chemie, Mumbai, India. Sodium dodecyl sulfate (SDS, $\geq 90.0\%$) was purchased from Merck, Mumbai, India. Polyoxyethylene sorbitan monolaurate (TWEEN-20, density-1.110 g/cm³ at 20°C) was obtained from Merck, Mumbai, India.

Standard stock solutions (1.0 mM) of surfactants were prepared using double-distilled water, and the desired concentrations of surfactant solutions were prepared by appropriate dilution of the standard stock solutions. Sodium hydroxide and hydrochloric acid (1.0 M) were used for pH adjustment. The required concentration of citrate-reduced silver nanoparticles (Ag NPs) was prepared by appropriate dilution of the 1.0 M stock solution of Ag NPs.

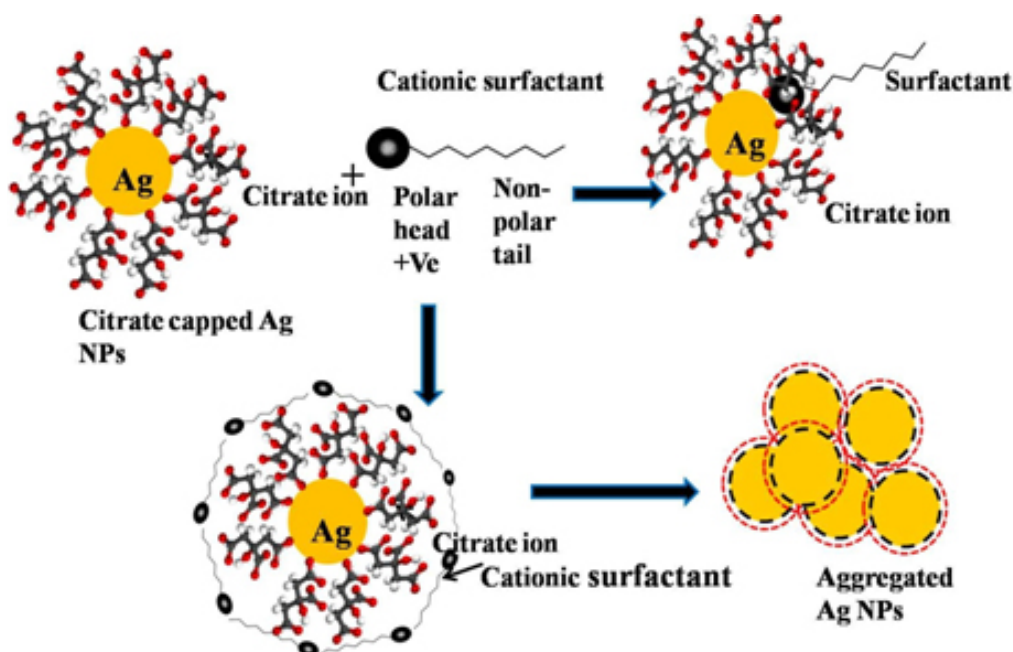
Procedure for preparation of citrate-reduced silver nanoparticles

Citrate-reduced Ag NPs were prepared according to a previously reported method^{34, 35} with

minor modifications: a 50 mL solution of 0.1 M AgNO₃ in a conical flask covered with foil paper was heated to boiling temperature. The solution was removed from the heating element and placed in an ice bath. Then, 5 mL of 1% sodium citrate solution (double-distilled water) was added dropwise with vigorous stirring. A pale yellow color appeared. The solution was then heated to boiling temperature with vigorous stirring. After completion of the reaction, the solution was cooled to room temperature under vigorous stirring, and a dark yellow color appeared. The final product was stored in a dark brown bottle at room temperature.

Sample preparation

Pharmaceutical samples such as commercial mouthwash (Cepacol, Australia; Fluocaril, Thailand) gum astringent (Stolin; India) and nasal spray (SinoFresh® Homeopathic Sinus and Nasal Care Spray; India) were prepared for the analysis. A 5.0 mL sample was transferred to a 100 mL volumetric flask and diluted 100 times with double-distilled water³⁶. Then, 1.0 μ L of the sample was subjected to NDS measurements. The water samples were collected from different areas of Raipur city, Central India, and were filtered with Whatmann-



Scheme 1: Schematic mechanism for cationic surfactants inducing the aggregation of citrate-capped silver nanoparticles

42 paper and analyzed in the laboratory. The proposed method was used for field experiments. Batteries were used as the energy source for the NDS instrument.

Procedure for the determination of cationic surfactants and spectral studies

Various CS solutions with a given concentration were added separately to an Ag NP

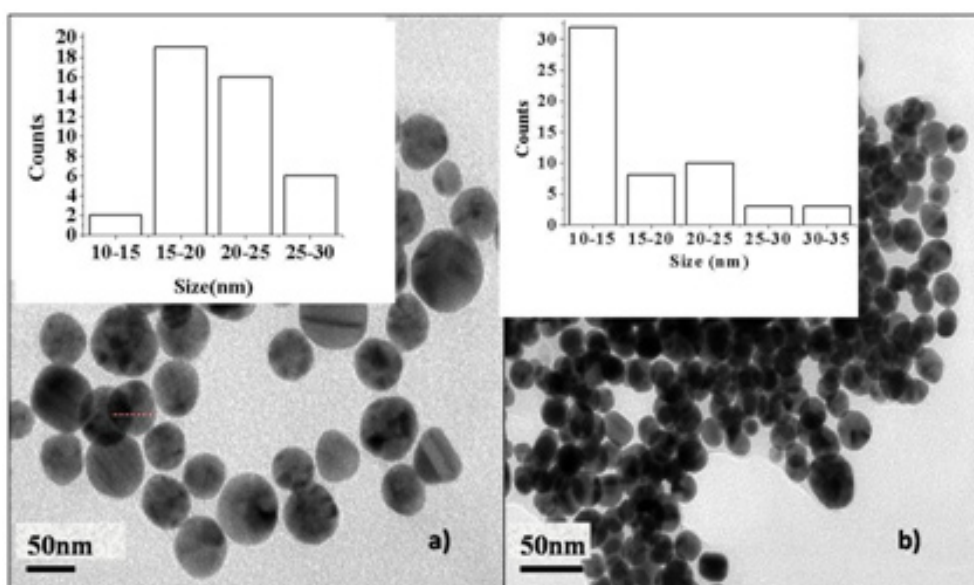


Fig. 1: High-resolution transmission electron microscopic images of silver nanoparticles a) before and b) after the addition of 1.0 μM cetyl pyridinium chloride

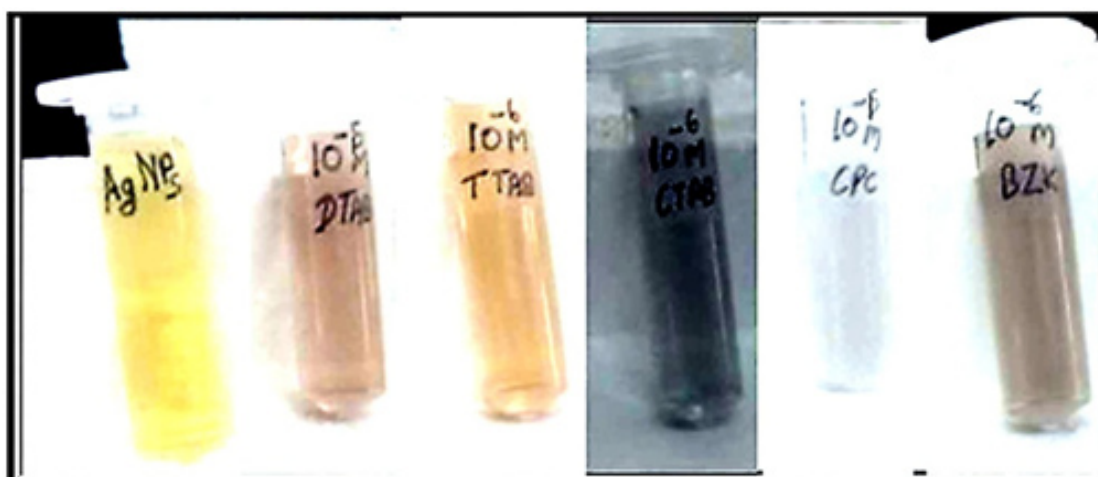


Fig. 2: The color change in the solution of silver nanoparticles after the addition of 1.0 μM of different cationic surfactants such as dodecyl trimethyl ammonium bromide, myristil trimethyl ammonium bromide, cetrimonium bromide, cetyl pyridinium chloride, and benzalkonium chloride

solution containing 10^{-3} M HNO_3 at room temperature. The absorption spectra and images were recorded 3 mins after adding the analytes, and 1.0 μL samples of the solutions were directly spotted onto the pedestal of the NDS for analysis of the absorption spectra.

RESULTS AND DISCUSSION

Characterization and aggregation of silver nanoparticles (high-resolution transmission electron microscopic analysis)

The Ag NPs were synthesized by the citrate reduction method with trisodium citrate. The HR-TEM

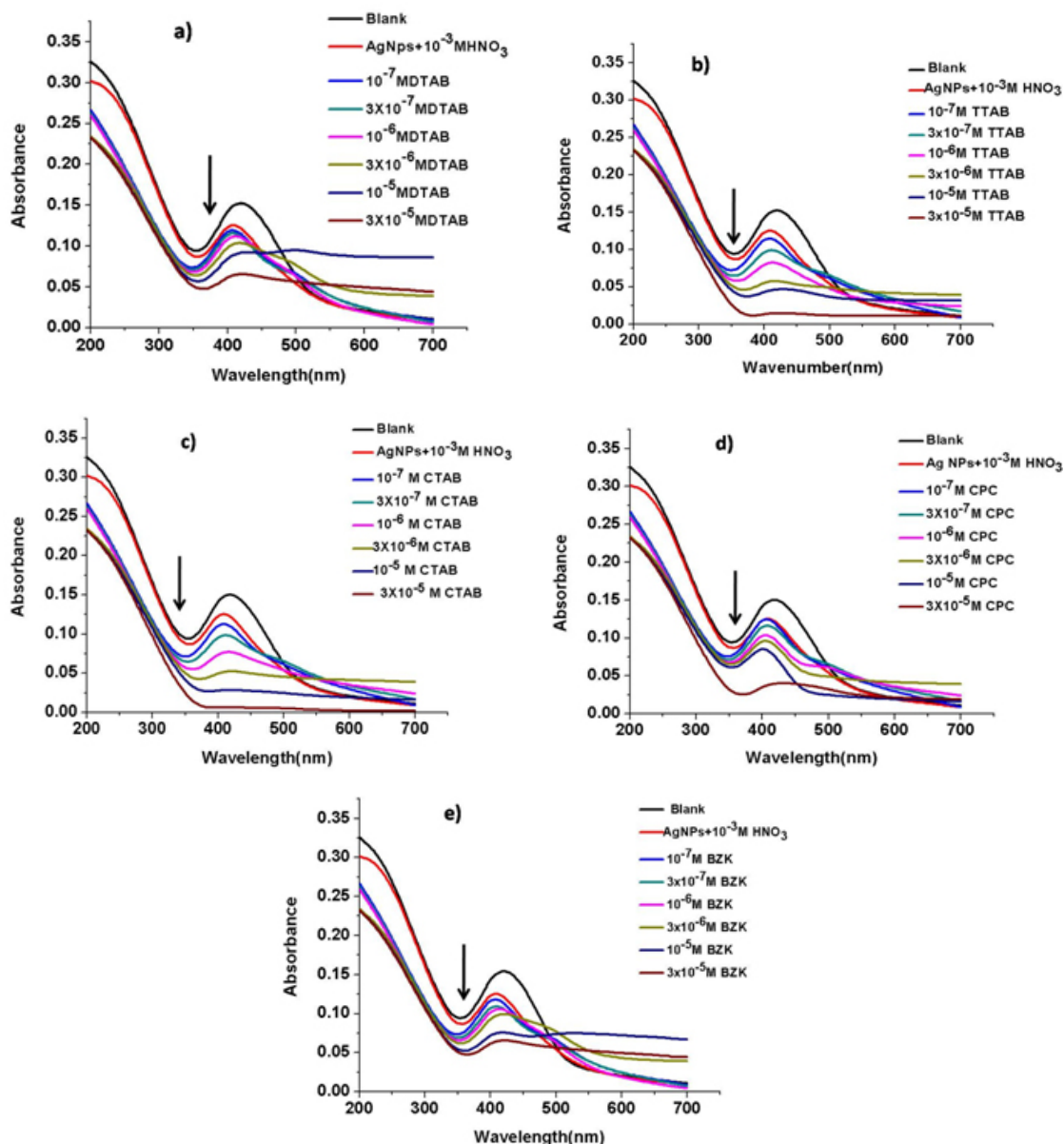


Fig. 3: Absorption spectra of the silver nanoparticle suspension ($\text{pH}=3.0$, 10^{-3} M HNO_3) in the presence of different concentrations of a) dodecyl trimethyl ammonium bromide(DTAB), b) myristil trimethyl ammonium bromide(TTAB), c) cetrimonium bromide(CTAB), d) cetyl pyridinium chloride(CPC), and e) benzalkonium chloride(BZK) in the range of 0.1-30 μM

images of dispersed Ag NPs and aggregated Ag NPs are shown in figure 1. According to the TEM analysis, the particle size of Ag NPs was 10.75 nm, which increased to an average size of 21.0 nm (calculated by histogram analysis) due to instantaneous aggregation of the NPs after the addition of 1.0 μM CPC.

The citrate-capped Ag NPs were highly sensitive to CSs. As shown in figure 2, when 1.0 μM of DTAB, TTAB, CTAB, CPC and BZK was added separately to the Ag NPs solution, the color of the solution changed from the yellow to colorless within 3 min, indicating the aggregation of Ag NPs.

Nanodrop spectroscopy

To investigate the effects of surfactants on Ag NPs through the absorption spectra, the whole experiment was performed on NDS. Figure 3 a, b, c, d, and e show that the absorption wavelength of the Ag NPs sharply decreased and that the absorption spectra gradually broadened to a longer wavelength with the addition of CSs.

Fourier transform infrared analysis of silver nanoparticles and cationic surfactants

As shown in figure 4, the OH stretching band at 3453.82 cm^{-1} in the FT-IR spectra of the Ag

NPs without surfactant shifted to 3453.22 cm^{-1} for the Ag NPs with a cationic surfactant (CPC), and a decrease in the OH peak is clearly visible. Similarly, the C=O peak at 1637.27 cm^{-1} in the Ag NPs shifted and decreased with the addition of CSs. The above changes in peaks confirmed the aggregation of Ag NPs.

Optimization of reaction conditions

Effect of pH

The effect of pH on the sample solution was investigated to obtain the optimal aggregation for Ag NPs. The optimal pH of the aqueous solution was investigated in the range of pH 2.0-10.0. The absorbance of the Ag NP solutions with the addition of 1.0 μM CSs was individually studied for each CS. The absorbance decreased as the pH increased to 3.0. Thus, pH 3.0 resulted in the optimal aggregation of Ag NPs, and above this pH, precipitation occurred. Therefore, pH 3.0 was chosen as the optimal pH for the whole study, as shown in figure 5.

Effect of different acids

To investigate the effect of different acids on the aggregation of Ag NPs with CSs, the absorption spectra of Ag NPs with CSs in the presence of 10^{-3}M different acids, such as H_2SO_4 , HCl, and HNO_3 , were analyzed. There was no any change in absorption

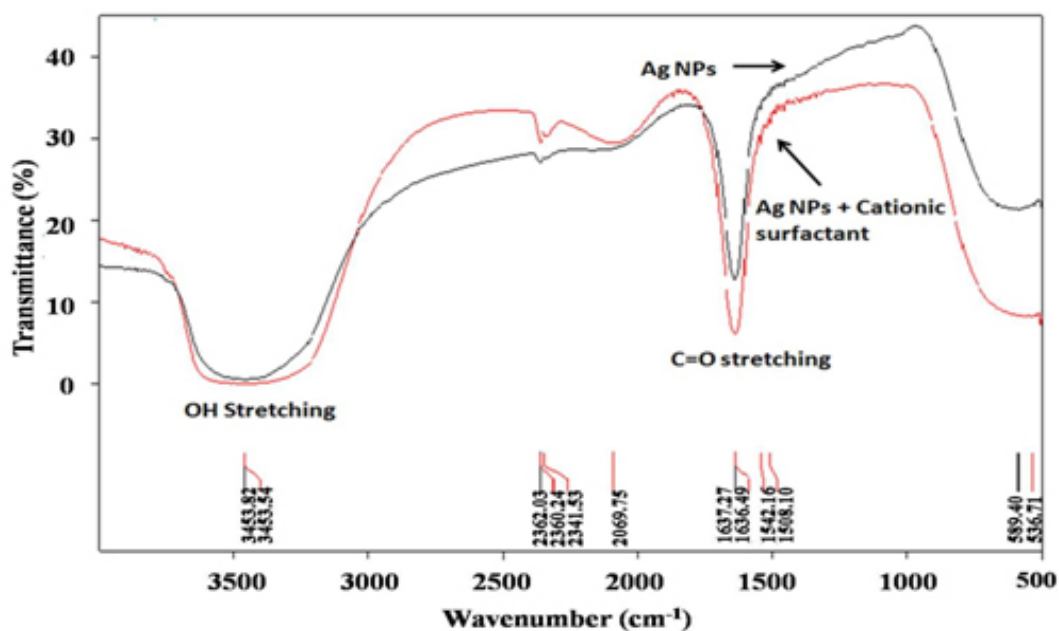


Fig. 4: Fourier transform infrared spectra of silver nanoparticles and silver nanoparticles-cationic surfactant (CPC) conjugate

spectra of Ag NPs by adding 10^{-3} M H_2SO_4 . The absorption spectra of Ag NPs decreased to a greater extent after the addition of CSs in the presence of 10^{-3} M HNO_3 than in the presence of 10^{-3} M HCl. The decrease in absorption spectra of the Ag NP solution at 400 nm is due to the aggregation of Ag NPs induced by CSs because of the strong size-dependent surface plasmon resonance properties of Ag NPs and also the molecular volume of NO_3^- ions is greater than that of Cl^- ions, the hydrophobicity of the ion pair formed by NO_3^- with CSs is stronger than the ion pair of Cl^- with cationic surfactants. Thus, 10^{-3} M HNO_3 was chosen as the optimal experimental condition³⁷⁻³⁸.

Effect of reaction time

The reaction time was the most important parameter of the experiment and was investigated in the range of 20-260 seconds under the optimized conditions. The absorbance of the Ag NP solution with CSs gradually decreased up to 180 sec and then remained constant. Thus, 180 sec (3 min) was selected as the optimal reaction time for the experiment and was sufficient for completion of the reaction.

Effect of salt concentration

Salt plays key role in aggregation of Ag NPs. Thus the influence of NaCl, $NaNO_3$, Na_2SO_3 , Na_3PO_4

and Na_2SO_4 on the aggregation of Ag NPs was also studied. The effect of various salts on Ag NPs with CSs was investigated separately in the range of 1.0×10^{-3} - 5.0×10^{-3} M under optimized conditions. However only NaCl gave the best results. The reason behind this phenomenon is electrostatic interaction between chloride ion and cationic surfactants adsorbed on the Ag NPs surface. Chloride is the best bridging ligands amongst another anions due to its medium size. Due to high absorbance below 2.0×10^{-3} M concentration, aggregation of Ag NPs was not be clearly visible beyond 2.0×10^{-3} M concentration of NaCl and absorbance remained constant. Thus, 2.0×10^{-3} M concentration of salt solution was used for the optimization of the experiment.

Effect of the concentration of the probe solution

The optimal concentration of probe solution (Ag NPs) was investigated by measuring the absorption intensity of probe solution Ag NPs in the presence of cationic surfactants under optimized condition. The effect of concentration of Ag NPs was studied in the range of 0.02-0.7 M. As the concentration of Ag NPs varied from 0.05-0.5 M, the absorbance was increased concurrently to 0.30M and beyond this absorbance remained constant. Therefore, 0.30M Ag Nps was sufficient

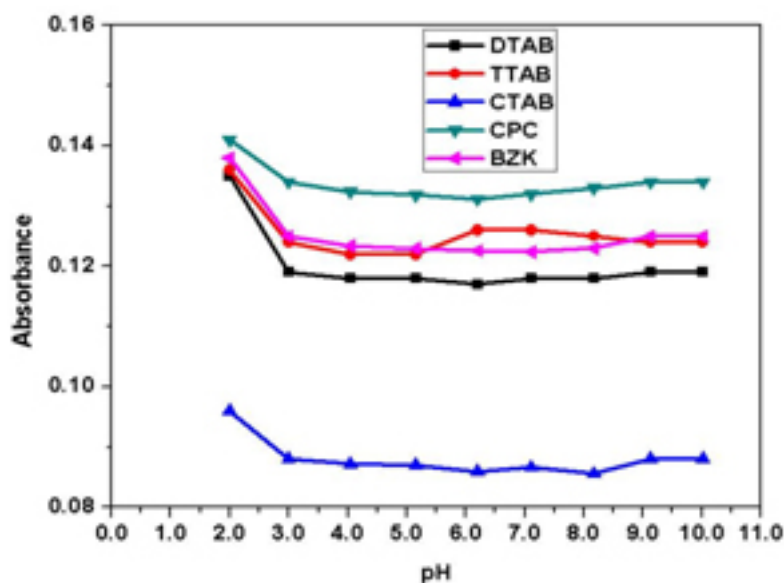


Fig. 5: Effect of pH on the aggregation of silver nanoparticles and cationic surfactants under optimized conditions

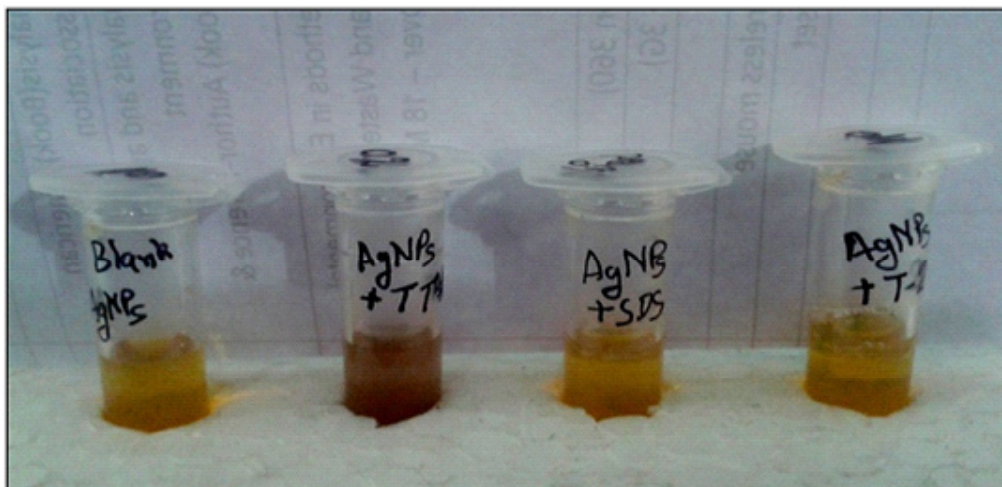


Fig. 6: Colorimetric response of silver nanoparticle solution ($\text{pH}=3.0$, 10^{-3} M HNO_3) upon the addition of $1.0 \mu\text{M}$ of various surfactants such as cationic (myristil trimethyl ammonium bromide, TTAB), anionic (sodium dodecyl sulfate, SDS) and nonionic (polyoxyethylene sorbitan monolaurate, T-20)

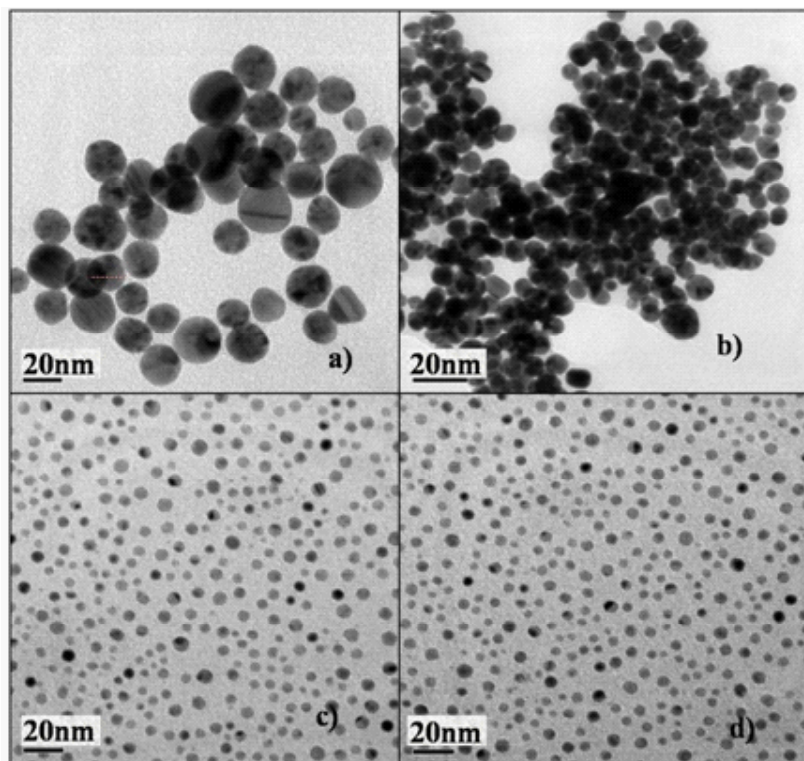


Fig. 7: High-resolution transmission electron microscopic analysis of silver nanoparticles a) before and b) after the addition of $1.0 \mu\text{M}$ cationic surfactant (aggregation), c) $1.0 \mu\text{M}$ anionic surfactant (no aggregation), and d) $1.0 \mu\text{M}$ nonionic surfactant (no aggregation)

Table 1: Determination of cetyl pyridinium chloride in commercial mouthwash, gum astringent, nasal spray pharmaceuticals by the proposed method

Pharmaceuticals	Cetyl pyridinium chloride ($\mu\text{g/mL}$)			Original sample ^b ($\mu\text{g/mL}$)
	Added	Found ^a	Recovery% ^c	
Cepacol	0	5.11 ± 0.78	101	511 ± 1.95
	3	8.98 ± 0.67	102	
	6	10.6 ± 0.56	95	
	9	13.2 ± 0.51	101.2	
Fluocaril	0	4.88 ± 0.96	97.4	488 ± 1.98
	3	7.96 ± 0.88	97.7	
	6	11.6 ± 0.68	103	
	9	14.1 ± 0.48	102	
Stolin	0	4.91 ± 0.96	98.5	491 ± 1.78
	3	6.99 ± 0.87	101	
	6	11.2 ± 0.68	102	
	9	12.8 ± 0.55	96.4	
Sinofresh	0	5.09 ± 0.37	96.4	509 ± 1.22
	3	8.06 ± 0.58	101.1	
	6	10.5 ± 0.48	98.9	
	9	12.9 ± 0.91	99.7	

^aAverage of three determinations \pm standard deviations,

^bAmount measured by the proposed method for mouthwash

^cCalculated by the formula $[(a+b=c)]$, $[(c-a/b)*100=\% \text{ Recovery}]$

Table 2: Determination of cetyl pyridinium chloride in environmental samples by the proposed method compared with previous methods

S. No.	Water Samples	Present Method [Using the Ag NPs method] (mgL^{-1})	RSD% n=6	Previous Method [Using Bi (III)] (mgL^{-1})	RSD% n=6
1	PW1	4.4	1.7	4.2	1.2
	PW2	3.5	1.2	3.8	1.3
2	GW1	1.7	1.1	1.9	1.3
	GW2	1.5	1.2	1.6	1.3
3	RW1	3.8	1.3	3.9	1.4
	RW2	3.6	1.3	3.5	1
4	MWW1	4.9	0.7	5	0.9
	MWW2	5.2	1.4	5.1	1.3

• PW=Pond Water, GW=Ground Water, RW=River Water, MW=Municipal Waste Water
Samples collected from Raipur City, Six analyses were performed

for aggregation of the Ag NPs solution with cationic surfactants.

Determination of different cationic surfactants

The sensitivity of the proposed work was investigated for the spectrophotometric determination of CSs, which were evaluated individually. The color change of the Ag NP suspension changed from yellow to red and finally to colorless with an increase in the concentration of surfactant. The CSs included several homologues with different lengths of alkyl chain. The limit of detection (LODs) were 15.0 μM , 8.0 μM , 6.0 μM , 13.0 μM , and 5.8 μM for DTAB, TTAB, CTAB, BZK and CPC, respectively. The LODs decreased with increasing surfactant chain size. With increasing concentration of cationic surfactants, the Ag NPs tended to redisperse because of the reversal of the surface charge of Ag NPs³⁹.

Selectivity

The selectivity of citrate stabilized Ag NPs was evaluated with the addition of different types of surfactants (cationic, anionic and non-ionic). CSs induced the aggregation of Ag NPs and change in color of Ag NPs solution was observed. Anionic surfactant SDS (sodium dodecyl sulphate) and non-ionic surfactant Tween-20 (Polyoxyethylene sorbitan monolaurate) could not induce the aggregation of Ag NPs with the addition individually and not change in color of Ag NPs was seen which was identified by experimental results and shown in figure 6. The selectivity of CSs surfactants was also proved by HR-TEM analysis as shown in figure 7.

Sensitivity, optimum concentration, and statistics

The proposed method is simple colorimetric determination. The LODs were 15.0 μM , 8.0 μM , 6.0 μM , 5.8 μM , and 13.0 μM for DTAB, TTAB, CTAB, CPC and BZK, respectively at λ_{max} 400nm. The % RSD was ± 1.2101 , ± 0.7134 , ± 0.8307 , ± 0.4983 and ± 1.1435 for DTAB, TTAB, CTAB, CPC and BZK, respectively. The optimum concentration of cationic surfactant was 1.0 μM at optimum pH 3.0 with 10^{-3}M HNO_3 .

Proposed work further extended for the determination of CPC in pharmaceuticals and

environmental samples. The calibration range, LOD and % RSD for CPC was 10^{-7} - $3 \times 10^{-5}\text{M}$, 5.8 μM and ± 0.4983 , respectively.

Application

The proposed method was successfully applied for the determination of CSs, such as CPC, in commercial mouthwash (Cepacol, Australia; Fluocaril, Thailand) gum astringent (Stolin; India) and nasal spray (SinoFresh® Homeopathic Sinus and Nasal Care Spray; India). Table 1 shows that the recoveries corresponding to the addition of varying concentrations of CPC to the sample solution was in the range of 95.0-103.0%. Additionally, there is good agreement between the results of the proposed method and the reference CPC content (500 $\mu\text{g/mL}$) of the mouthwash formulation. Triplicate measurements were performed in the consumer product analysis. The proposed method was tested for the analysis of CPC in environmental (water) samples. The bismuth (III) iodide method was used for data validation of the environmental samples (table 2).

CONCLUSION

In the present method, citrate-stabilized Ag NPs applied for the determination of CSs. The absorbance of the probe solution decreased upon the addition of surfactant solution due to the aggregation of Ag NPs. The proposed NDS method was simple, low cost, rapid and applicable for the on-site determination of surfactants. This method provides a simple colorimetric determination of CSs. The proposed method was successfully utilized for the determination of CPC in pharmaceutical such as commercial mouth washers, gum astringent, nasal spray and environmental samples, such as pond water, ground water and municipal waste water. After comparison of present method with previously reported method, the present method has found with better selectivity than previous methods.

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