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Article *in* Analytical Sciences · July 2016

DOI: 10.2116/analsci.32.769

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A Simple and Rapid Method Based on Anti-aggregation of Silver Nanoparticles for Detection of Poly(diallyldimethylammonium chloride) in Tap Water

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A simple and rapid method was developed for the detection of poly(diallyldimethylammonium chloride) (PDADMAC) using citrate-capped silver nanoparticles (AgNPs). Detection was based on anti-aggregation of AgNPs in phosphate buffer caused by PDADMAC. Due to its positive charges, PDADMAC was adsorbed onto AgNPs *via* electrostatic interaction with citrate, which resulted in the charges at the particle surfaces to become positive and caused repulsion among particles. Furthermore, long-chain PDADMAC provided steric hindrance. These two effects promoted the dispersion of AgNPs in the phosphate buffer. A change in the state of dispersion influenced the surface plasmon resonance (SPR) of AgNPs. Therefore, in this work, the concentration of PDADMAC was determined by monitoring changes in absorbance (at 396 nm) caused by SPR of AgNPs. Under optimal conditions, the calibration was linear over the range of 1 to 100 mg L^{-1} with a detection limit of 0.7 mg L^{-1}. Satisfactory precision was obtained (RSD = 2.8%). This method was successfully applied to the determination of PDADMAC in tap water samples. The recoveries ranged from 86.0 – 107.5%.

Keywords Anti-aggregation, poly(diallyldimethylammonium chloride), silver nanoparticles, tap water

(Received February 29, 2016; Accepted March 29, 2016; Published July 10, 2016)

Introduction

Poly(diallyldimethylammonium chloride) (PDADMAC), is a cationic quaternary-amine polymer frequently used as a coagulant in water and wastewater treatment.[1] Since PDADMAC is rich in positive charges, it can be used to neutralize and induce negatively charged species in suspension to sediment, resulting in clarification of water during treatment. Typically, excess PDADMAC is added to water to accelerate precipitation of suspended solids. Therefore, some residues of this compound are found in water after treatment. Although PDADMAC has low acute effects on human health compared to microbial contamination, long-term accumulation in living organisms and the environment is still a concern. PDADMAC can bind with DNA causing a conformational change in its structure.[2] It has been reported that residual PDADMAC can react with other chemicals used in water treatment processes to generate suspected carcinogens.[3,4] Consequently, monitoring this compound in water after treatment is very important in terms of safety and quality control.

PDADMAC concentrations can be determined by several methods, including titration[5] and spectrophotometry.[6] These methods are conceptually simple, but time-consuming and labor-intensive. Other techniques such as size-exclusion chromatography[7] and capillary electrophoresis[8] have been used for PDADMAC analysis. However, costly instrumentation and skilled technicians are required for these techniques.

A trend in nanotechnology is the use of colorimetric sensors based on exploiting the properties of metal nanoparticles (especially gold and silver). These have been extensively developed. The detection principle is generally based on particle aggregation triggered by a target analyte. Strategies have been presented for detection of various analytes, such as metal ions,[9] neutral molecules,[10] polymers[11] and surfactants.[12] However, some inherent challenges remain. In practical analysis, matrices in a sample may also induce aggregation of particles, giving positive errors in measurement. This problem often hinders practical applications of nanoparticle sensors. In order to avoid interference, detection based on anti-aggregation has recently been investigated.[13–16] Only a few species can inhibit the aggregation of particles, thereby improving the selectivity of nanoparticle sensors.

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In an anti-aggregation system, the aggregating agent is generally introduced as a colloidal nanosensor to induce particle agglomeration. The agglomeration process can be interrupted by a target analyte through specific mechanisms, thereby initiating the re-dispersion of particles. This approach has been proposed for analyzing copper[13] and mercury[14] in water as well as detected biothiols[15] in biological fluids. Recently, a method employing anti-aggregation with the use of no aggregating agent has been reported.[16] Agglomerated nanoparticles were simply prepared by dispensing the particles in a specified medium of a particular ionic strength. This method is much easier to use.

Up to date there has not been any reported use of silver nanoparticles (AgNPs) for detection of PDADMAC based on an anti-aggregation mechanism. In this work, citrate capped AgNPs were employed as a colorimetric probe for measurement of PDADMAC levels in tap water. The proposed method was used without an aggregating agent. Aggregation of AgNPs was simply triggered by dispersing the particles in a phosphate buffer. In the presence of polymeric PDADMAC, the polymer can be adsorbed onto particle surfaces *via* electrostatic attraction between its positive charge and negatively charged citrate. Particle surfaces subsequently become positive. AgNPs are then re-stabilized in the medium by cationic repulsive and steric forces of the adsorbed polymer. The degree of dispersion strongly affects the surface plasmon resonance (SPR) of nanoparticles. Therefore, quantification of PDADMAC can be performed by measuring the change in SPR of AgNPs, which is proportional to PDADMAC concentration.

Experimental

Chemicals

All chemicals were of analytical grade and used without further purification. Deionized water was used throughout the study. Silver nitrate was purchased from Carlo Erba (UK). Sodium borohydride and sodium citrate tribasic dihydrate were obtained from Sigma Aldrich (Germany). A standard solution of PDADMAC was prepared from 20 wt% poly(diallydimethylammonium chloride) (MW ~200000 – 350000), Sigma-Aldrich (USA).

Instruments

The morphologies of AgNPs were observed by transmission electron microscope (TEM) (Tecnai G^2 20, USA). The zeta potential of particle surfaces was determined using a zeta analyzer (Malvern Instruments, UK). The absorbance of AgNPs was monitored by a spectrophotometer (Jasco V-630, Japan).

Synthesis of AgNPs

A colloidal solution of citrate capped AgNPs was prepared according to a procedure described by Haghighi and Bozorgzadeh[17] with slight modification. Briefly, 5 mL of 1 wt% sodium citrate was added to 25 mL of 1 mM silver nitrate under vigorous stirring. After 10 min, 75 mL of 2 mM sodium borohydride was slowly dropped into the prepared solution. The solution was continuously stirred for another 20 min. A yellow colloidal solution of AgNPs was obtained. The resulting AgNPs solution was kept at 4°C for 2 days prior to use. This solution was stable for 1 month under refrigeration.

Standard preparation and the procedure for colorimetric detection of PDADMAC

A stock solution of 1000 mg L^{-1} of PDADMAC was prepared by diluting 2.4 mL of 20 wt% PDADMAC to 500 mL with DI water. A series of working standard solutions (1, 5, 10, 25, 50, 75 and 100 mg L^{-1}) was made by pipetting the appropriate amounts of stock solution into a 25-mL volumetric flask. A 20-mL volume of 0.2 M phosphate buffer (pH ~7.4) was then added into the flask. The solution was brought to its final volume with DI water.

For colorimetric detection of PDADMAC, 5 mL of individual standard solutions were mixed with 5 mL of AgNPs solution. The mixture was agitated using a vortex mixer for 1 min. The absorption spectrum of the resulting solution was recorded after 3 min of reaction.

Sample preparation and analysis

The proposed method aimed to analyze residual PDADMAC in treated water. Therefore, tap water from different sources was used as samples. Sample A was collected in an area supplied by a metropolitan waterworks authority (Bangkok, Thailand). Sample B was collected from a place serviced by a provincial waterworks authority in Northeastern Thailand.

In the procedure, a 3-mL sample was placed into a 25-mL volumetric flask. Subsequently, 20 mL of phosphate buffer was added, followed by adjusting the volume of solution to 25 mL with DI water. This sample was mixed with the AgNPs solution in a volume ratio of 5 mL to 5 mL. The SPR of the mixture was measured after 3 min.

Validation method

Metachromatic polyelectrolyte titration with spectrophotometric detection of the endpoint was used as a validation method.[5] A 50-mL solution of PDADMAC and 0.2 mL of toluidine blue O indicator were transferred into a 250-mL Erlenmayer flask. The titration was done by slowly dropping 0.2 mL of 0.5 g L^{-1} potassium salt of polyvinyl sulfate into the flask. At endpoint, the color of the indicator changed from blue to purple-pink. Absorption at a wavelength of 634 nm (the maximum absorption wavelength of the blue color indicator) was used to monitor the titration and determine the endpoint.

Results and Discussion

Characteristics of AgNPs

AgNPs were synthesized *via* borohydride reduction by using citrate as a stabilizing agent. The resulting particles had negative charges on their surfaces. A colloidal solution of AgNPs appeared yellow with a strong absorption peak at 396 nm. The morphologies of the particles were characterized by TEM. It was observed that the as prepared AgNPs were of spherical shape with an average diameter of 6 ± 2 nm.

Anti-aggregation mechanism of AgNPs by PDADMAC

AgNPs were well-suspended in DI water during their preparation. However, when the AgNPs were dispersed in phosphate buffer, the particles readily agglomerated. This was caused by a large number of ionic species in the buffer, effectively shielding particles from electrostatic repulsion.[18,19] The London-van der Waals force therefore played a major role upon the attraction among particles. This leads to reduced inter-nanoparticle distances, causing particle agglomeration. As a result, the color of the colloidal solution changed from yellow to purple grey (Fig. 1a, the first tube on the left). Agglomeration of particles in phosphate buffer was confirmed in a TEM image (Fig. 1b). However, in the presence of PDADMAC, aggregation of AgNPs was prevented. With increasing PDADMAC concentration, proportional dispersion of AgNPs was observed

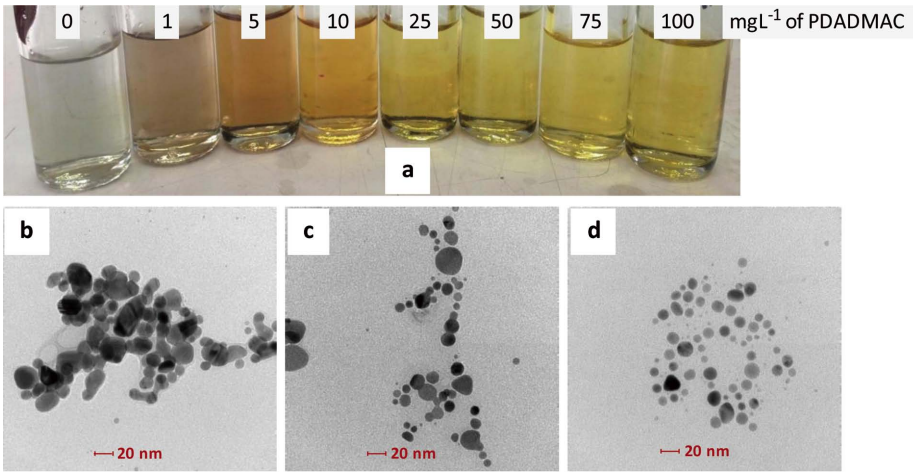

Fig. 1 (a) A color change of AgNPs dispersed in 0.2 M phosphate buffer (pH ~7.4) with addition of various concentrations of PDADMAC. TEM images of AgNPs in the buffer in (b) absence, (c) and (d) presence of 10 and 50 mg L^{-1} of PDADMAC, respectively.

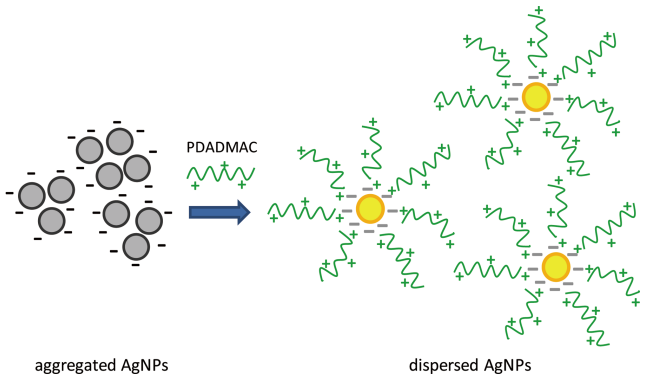

Fig. 2 Possible mechanism for PDADMAC anti-aggregating the citrate capped AgNPs in phosphate buffer.

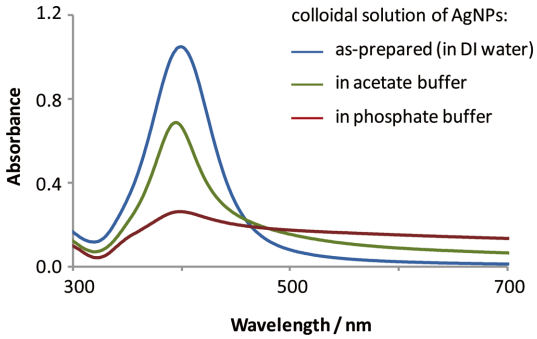

Fig. 3 The SPR absorption of AgNPs dispersed in 0.1 M phosphate buffer (pH ~3.2) and 0.1 M acetate buffer (pH ~3.6), compared with the as-prepared solution.

(Figs. 1c and 1d). Re-dispersion of agglomerated AgNPs by PDADMAC can be explained. PDADMAC is a cationic quaternary-amine polymer with abundant positive charges. When introducing PDADMAC into an agglomerated AgNP suspension, the polymers are attached to the particle surfaces due to electrostatic attraction between their positive charges and the negatively charged citrate stabilized particles.[12] The attached polymers afforded a double layer of positive charges around the particles (Fig. 2), leading to further repulsion between particles. Moreover, the long-chain polymer enhanced steric hindrance. The attached PDADMAC acted as a barrier, preventing contact with neighboring particles.[20] AgNPs were well dispersed in the phosphate buffer due to these electrostatic and steric effects. As a result, the color of the AgNPs solution turned from purple-grey to yellow as the degree of particle dispersion increased (Fig. 1a). Based on these findings, AgNPs could thus be used as a colorimetric probe for quantification of PDADMAC.

In order to confirm this anti-aggregation mechanism, the zeta potential of particle surfaces was monitored using a zeta analyzer. It was found that the zeta potentials of AgNPs in phosphate buffer in the presence of 0, 25, 50 and 100 mg L^{-1} of PDADMAC were –18.5, 3.2, 4.0 and 6.1 mV, respectively. The potential at particle surfaces changed from negative to positive values after the addition of PDADMAC, implying the formation of a double layer of PDADMAC on AgNP surfaces.

Optimization

The type of working medium strongly influenced the stability of nanoparticles,[12,21] which affected the intensity and position of their SPR peaks. SPR characteristics of these AgNPs in different media, *i.e.*, 0.1 M phosphate buffer (pH ~3.2) and 0.1 M acetate buffer (pH ~3.6), were studied. Figure 3 shows SPR absorption of AgNPs dispersed in phosphate and acetate buffers, compared to the as-prepared colloidal solution. It was found that the highest degree of agglomeration was attained when particles were dispersed in phosphate buffer, with the lowest SPR absorption at 396 nm and broadest shoulder. Based on the proposed anti-aggregation system, agglomeration of AgNPs is desirable (absence of PDADMAC), hence phosphate buffer was selected as the working medium.

The pH of the solution may not significantly affect the quaternary amine, PDADMAC, but this factor often contributes to the stability of nanoparticles. Therefore, the effect of phosphate buffer with pH values at 3.2, 7.4 and 12.0 was examined. It was found that a solution with pH at 3.2 gave poorer detection of PDADMAC, while pH values of 7.4 and 12.0 offered better sensitivity. This is because citrate, acting as

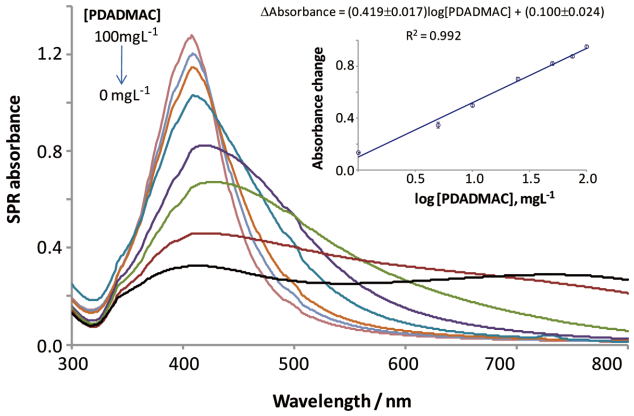

Fig. 4 The SPR spectrum of AgNPs in 0.2 M phosphate buffer at pH of 7.4 with various concentrations of PDADMAC (0, 1, 5, 10, 25, 50, 100 mg L^{-1}). Inset is a calibration plot.

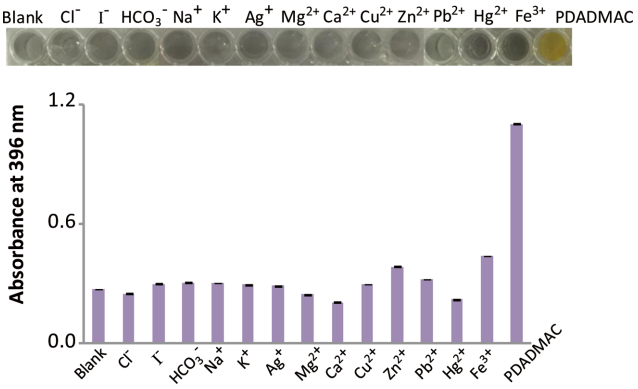

Fig. 5 A change in color and absorbance of AgNP solutions treated with 25 mg L^{-1} of PDADMAC and other ions at the same concentration.

a particle stabilizer, has three pK_a values, 3.1, 4.7 and 6.4. At a pH value of 3.2, two carboxylates are protonated, decreasing the negatively charged stabilized particle surfaces. This allowed for low attraction of PDADMAC to the particle surfaces. Therefore, repulsion due to positive charges and steric effects by adsorbed polymer upon AgNP surfaces may not be enough to aid in particle dispersion, causing poor sensitivity of AgNPs to PDADMAC. Alternatively, at pH values of 7.4 and 12.0, all carboxylates are definitely deprotonated. These two conditions provided for more negative charges on particle surfaces, which facilitated PDADMAC becoming surrounding by AgNPs. As a result, particle suspension could be easily recovered in the presence of a low concentration of PDADMAC. This means that the method had good analytical sensitivity. In this work, phosphate buffer with a pH at 7.4 was selected for the assay.

Buffer concentration of the solution also played a role in aggregation of AgNPs. Various concentrations of phosphate buffer (pH ~7.4) were tested, 0.01, 0.05, 0.10 and 0.20 M. It was found that 0.01 M phosphate buffer could not induce aggregation of AgNPs. Phosphate buffer concentrations in the range of 0.05 to 0.20 M provided the same level of AgNPs aggregation, facilitating comparable sensitivity for PDADMAC detection. In this work, 0.2 M phosphate buffer was chosen as the optimal medium.

Reaction time of AgNPs and PDADMAC at ambient temperature was determined by monitoring changes in SPR absorption of mixture solutions at 396 nm. It was found that SPR absorption increased rapidly and then remained constant after 1 min. This implied that the anti-aggregation of AgNPs by PDADMAC proceeded very quickly. In the current study, absorbance measurements were performed after 3 min of reaction since batchwise experiments are more conveniently done. The method under study offered rapid analysis compared to the other methods, including titration,[5] spectrophotometric[6] and chromatographic[7,8] methods.

Analytical performance

The developed colorimetric method relied on PDADMAC to hinder aggregation of colloidal AgNPs and lead to the resulting increase in SPR absorption by AgNPs. From Fig. 4, it can be seen that the absorbance intensity of AgNPs at 396 nm increased proportionally with the concentration of PDADMAC. In some situations, a logarithmic relationship between the response signal and concentration of analyte (log C) was used for quantitative analysis.[22-24] The results showed that a calibration, which plotted signal and log C, provided satisfactory performance for quantitative analysis. In this work, a calibration curve was constructed by plotting the change in absorbance intensity against the logarithmic PDADMAC concentration. Under the optimal conditions given above, a linear relationship was obtained over the range of 1 to 100 mg L^{-1} PDADMAC (inset of Fig. 4). The regression equation is:

$$\text{Absorbance change} = (0.419 \pm 0.017)\log[\text{PDADMAC}] + (0.100 \pm 0.024)$$

The R^2 of this regression was 0.992. The limits of detection (LOD) and of quantitation (LOQ) were calculated on the basis of 3 and 10 times the standard deviation of a blank signal (five measurements), respectively. LOD of 0.7 mg L^{-1} and LOQ of 1.0 mg L^{-1} were achieved. Precision of the developed method was calculated as the relative standard deviation (RSD) of five measurements of a blank solution. As a result, good precision (2.8% RSD) was attained.

Selectivity

The selectivity of the method toward PDADMAC was evaluated by testing the colorimetric response of the AgNP sensor to other environmental ions. Under optimal conditions, 25 mg L^{-1} of all tested ions, including PDADMAC, were separately spiked into the AgNP solution. As illustrated in Fig. 5, an obvious color change was observed in the presence of PDADMAC, while other ions did not show this effect. Absorbance of the AgNP solution at 396 nm sharply increased only after the addition of PDADMAC, whereas slight variations of absorbance were observed for other ions tested. This showed that other ions could not promote dispersion of aggregated AgNPs in phosphate buffer. As a result, the assay developed in the current study was satisfactorily selective to PDADMAC and not impacted by other common ions.

Analysis of tap water samples

In order to verify the applicability of the method to real samples, tap water from different sources were analyzed. Metachromatic titration[5] was employed for validation. The results are given in Table 1. Using the paired t-test statistic, there were no systematic differences between the results obtained using these two methods ($t_{observed}$ = 0.13, $t_{critical}$ = 4.30, p = 0.05). Recovery was studied using samples spiked with

Table 1 Determination of PDADMAC in tap water using the anti-aggregation method of the current study and titration method

Sample	PDADMAC/mg L^{-1}		
	Added	Found	
		Anti-aggregation method	Titration method[5]
A	—	n.d.	n.d.
	25.0	23.9 ± 1.5	22.3 ± 0.3
	40.0	38.6 ± 0.9	38.1 ± 0.6
B	—	n.d.	n.d.
	5.0	4.3 ± 0.0	8.2 ± 0.1
	40.0	43.0 ± 0.4	38.7 ± 0.4

n.d. = not detectable.

different amounts of PDADMAC. It was found that the recoveries were in the range of 86.0 to 107.5%. These results indicate reliability of the anti-aggregation method developed for quantification of PDADMAC in water samples without interference of other factors.

Conclusion

A new colorimetric method based on AgNP sensor for detecting PDADMAC was developed. Positively charged PDADMAC interacted with negatively charged citrate capped AgNPs, causing cationic repulsion and steric polymer hindrance among particles. This effectively enhanced anti-aggregation of AgNPs in phosphate buffer and their re-dispersion in that solution. The AgNP sensor was used as prepared with no surface modification, resulting in a much simpler procedure. Moreover, the method developed in the current study allowed for rapid analysis, enabling higher throughput than can be obtained with conventional titration,[5] spectrophotometric[6] and chromatographic[7,8] methods. The corresponding anti-aggregation system was applied to quantitative analysis of PDADMAC in tap water. Successful application of this method to analyze tap water revealed the potential of this method for determination of residual PDADMAC in water supplied by waterworks.

Acknowledgements

This work was financially supported by the Thailand Research Fund (MRG5980008).

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