Chemical Science Review and Letters ISSN 2278-6783

Research Article

Study of the Stability of Silver Particles Suspended using Cetylpyridinium Bromide (CPB) as Surfactant

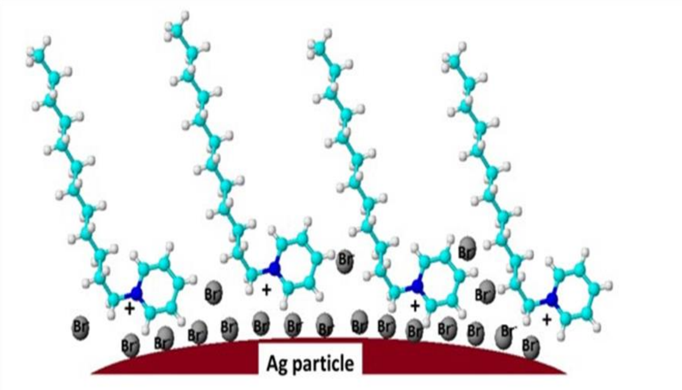
Sandra G. González-Arellano[1], Luz Ma. Reyna Avilés-Arellano[2], Juan Manríquez[1], Julieta Torres[1], Raúl Ortega[1], Yunny Meas[1], Gabriel Trejo[1], and Alia Méndez-Albores[3,*]

[1]Center of Research and Technological Development in Electrochemistry (CIDETEQ), Parque Tecnológico Sanfandila, Pedro Escobedo, Querétaro, A.P. 064. C.P. 76703, México
[2]Cinvestav-IPN, Unidad Querpetaro; Libramiento Norponiente #2000 Fracc. Ral de Juriquilla, Querétaro, C.P. 76230, México
[3]Center of Chemistry-ICUAP Benemérita Universidad Autónoma de Puebla, Ciudad Universitaria Puebla, 72530 Puebla, México

Abstract

Stable suspensions of Ag particles were prepared using cetylpyridinium bromide (CPB) as surfactant. The stability was evaluated using a Turbiscan optical analyzer, and the delta transmittance data showed that increasing the concentration of CPB in the suspension significantly enhanced the stability. Additionally, for CPB concentrations in the range of 0.1 to 5 mM, the Z-potential values of the suspension increased. For concentrations higher than or equal to 5 mM CPB, the Z-potential values remained constant. CPB-Ag particle interactions were studied by Raman spectroscopy, and the results suggested that the CPB surfactant molecule is adsorbed with the ionic (-N+C5H5) head group oriented toward the Ag surface and the hydrophobic tail directed away from the surface. Additionally, coadsorbed Br- ions are very important for binding in the first monolayer. The pyridinium head groups are surrounded by bromide ions, and the pyridinium/ bromide system is strongly adsorbed onto the Ag surfaces surfaces.

Keywords: adsorption, Cetylpyridinium Bromide, Raman spectroscopy, Silver particles.



Schematic representation of cetylpyridinium bromide surfactant adsorption on silver particles

***Correspondence**
Author: Alia Méndez-Albores
Emails: alia.mendez@correo.buap.mx

Introduction

In recent years, inorganic antibacterial agents have attracted the attention of researchers because of their thermal resistance and the persistence of their antibacterial effects compared with those of organic antibacterial agents [1]. Since the nineteenth century, silver (Ag)-based compounds have been used in many antimicrobial applications; colloidal silver was used in wound antisepsis and in combination with citrate salts for the treatment of skin infections, and silver nitrate was employed almost 100 years ago for the treatment of ophthalmia neonatorum [2]. Currently, Ag nanoparticles are used in numerous physical, biological, and pharmaceutical applications. The antibacterial properties of silver particles against Gram-negative and Gram-positive bacteria have been widely demonstrated [3-7]; for this reason, silver particles (AgPs) are used in a large variety of applications, such as athletic apparel, washing machines, food-packaging materials [8, 9], and, most importantly, in the medical field as bactericidal and therapeutic agents. AgPs are used in the fabrication of dental devices, as bactericidal coatings in water filters, and as antimicrobial agents in air sanitizer sprays, pillows, respirators, socks, wet wipes, detergents, soaps, shampoos, toothpastes, and many other consumer products. AgPs are also used as antimicrobial agents in many public places such as railway stations and elevators in China, and they are believed to have good antimicrobial activity. Although silver particles offer various benefits, primarily as a result of their beneficial antibacterial properties [10, 11], there is also the problem of the nanotoxicity of silver. Various studies in the literature suggest that nanoparticles can cause various environmental and health-related problems [12, 13]. Nevertheless, there is a need for more studies to be conducted before it can be unequivocally concluded that the use of silver nanoparticles poses a significant problem.

On the other hand, during the fabrication process of many products containing AgPs as an antibacterial agent, a stable dispersion of the AgPs in an aqueous solution is required. The modification of a solid surface via the adsorption of a water-soluble polymer is an efficient and widely employed method of enhancing the dispersion stability of a suspension [14, 15]. Electrostatic and steric mechanisms are typically considered to be responsible for the stabilization of suspensions. Because of its spatial structure and hydrophilic functional groups, adding a surfactant can enhance the electrostatic repulsion and steric hindrance between AgPs. In recent years, the applications of surfactants have extended to the field of nanotechnology, where they are used as powerful tools for the preparation and modification of nanoparticles [16, 17].

The main focus of this study has been to investigate the stability of AgPs in an electrolytic bath for Cr electrodeposition, in the presence of a cationic surfactant (cetylpyridinium bromide (CPB)), using a dispersion-stability analyzer. To determine their surface charge, Z-potential measurements were performed, and the interactions between the AgPs and the cationic surfactant were analyzed using Raman spectroscopy.

Experimental

Stability analyses

The following procedure was used to analyze the influence of the surfactant CPB on the stability of AgPs in an electrolytic bath. First, 0.0625 g of AgPs (99.9%, 50-60 nm, SkySpring Nanomaterials, Inc.) was weighed and added to 25 mL of a base solution S_0 (electrolytic bath) at pH = 5.0 that contained the following: 107 g L^{-1} $CrCl_2 \cdot 6H_2O$ + 23 g L^{-1} NaCl + 50 g L^{-1} H_3BO_3 + 24 g L^{-1} HCOONa + 21 g L^{-1} NH_4Cl. Next, the surfactant CPB (98%, Spectrum Labs, USA), was added to the solution at the desired concentration (mM) at a given pH value for the evaluation of the long-term dispersion stability. Several concentrations of CPB in the electrolytic bath were tested, the concentrations were selected in the range of lower and higher concentrations than the critical micelle concentration (c.m.c.) of CPB in high ionic strength aqueous solutions (c.m.c. ~ 1 mM) [18, 19]. The aqueous suspension of AgPs was placed into cylindrical glass tubes and set into a Turbiscan Lab Expert analyzer (Formulation Co., L'Unión, France). The Turbiscan Lab Expert allows the measurement of the long-term stability of opaque and concentrated colloidal dispersions in addition to evaluate the size of the suspended particles and detecting instability much earlier and more easily than can be accomplished with the naked eye [20]. The sensors for transmitted and backscattered light in this optical analyzer scanned the entire height (50 mm) of the aqueous AgPs suspension (25 mL) for 24 h. The stability analysis of the aqueous AgPs suspension was performed based on the transmission (ΔT) and backscattering (ΔBS) profiles shown in **Figure 1**. The thickness of the clarifying layer (ΔH) in the clarifying zone can be calculated from the transmittance graph using the TLAB EXPERT software. In this software, the user defines the % transmittance; the software then determines the positions with respect to the length of the vial ($H_{d\text{-sup.}}$ and $H_{d\text{-inf.}}$) for each scan performed (see Figure 1a). The distance ΔH (mm) with respect to the length of the vial between the two values ($\Delta H = H_{d\text{-sup.}} - H_{d\text{-inf.}}$) defines the extent of the precipitation of the AgPs. Small values of ΔH indicate a stable suspension, whereas large values indicate an unstable suspension.

Z-potential measurements

Z-potential measurements were performed using an AcoustoSizer IIs (Colloidal Dynamics Inc.). In general, duplicate samples were measured four times each at 25°C. However, the reported Z-potential values for the AgPs-surfactant complexes are the results from a single sample measured four times. The deviation in the Z-potential between independent samples varied by 5%, but the trend was the same.

Raman Spectroscopy

The Raman spectra were recorded using a Thermo-Scientific Raman spectrometer (Mod. DXR) with a 780-nm diode laser source and a real output power of 10 mW. The laser was focused onto a 1.5-µm spot of the sample, using an Olympus optical microscope with an objective lens magnification of 20X, and the scattering signal was collected at 180°. Four spectra of each freshly prepared solution were obtained.

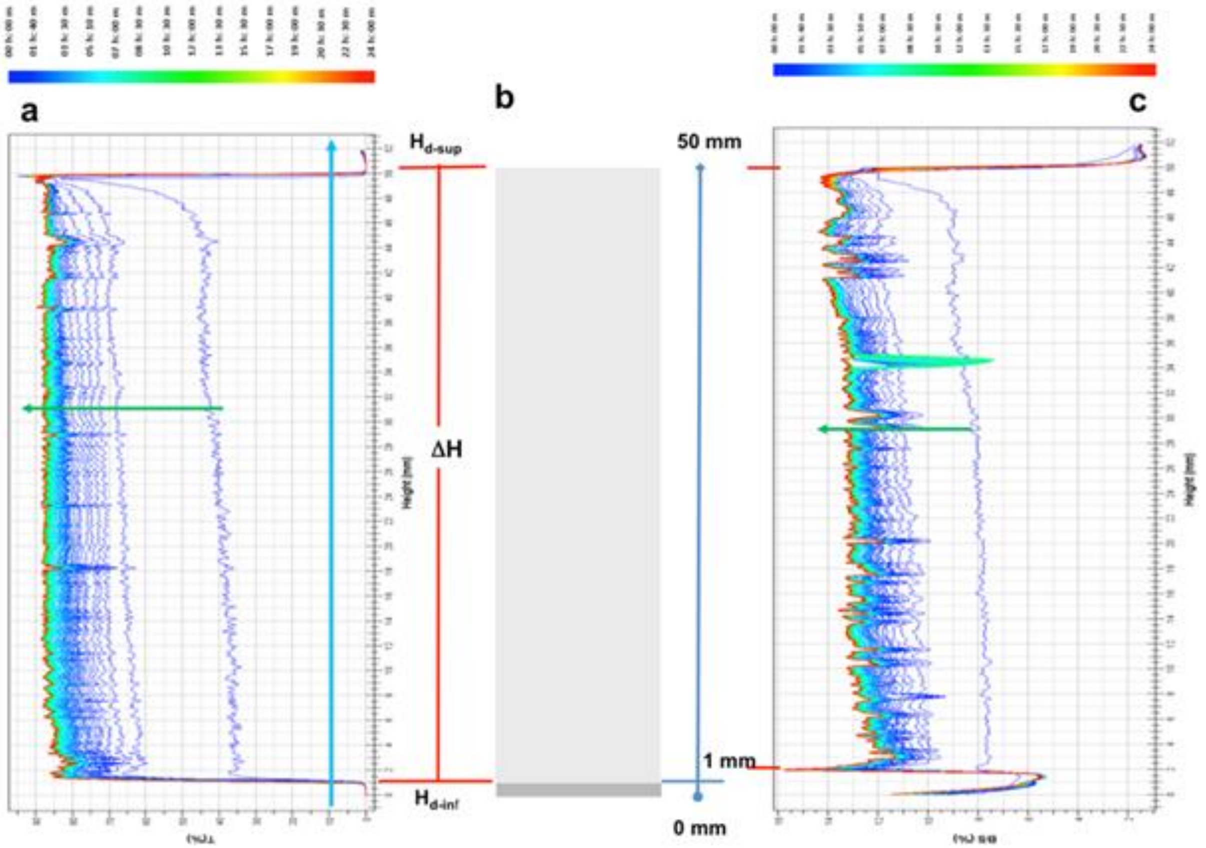


Figure 1 (a) Transmission and (c) backscattering profiles typical of an electrolytic bath of Cr with silver particles (AgPs) and without the surfactant CPB. The data are reported as a function of time (0 to 24 h) and sample height (0 to 50 mm).

Results and Discussion

AgPs-suspension stability measurements

The stability of the AgPs suspended in solution was measured using a dispersion-stability analyzer. The stability tests were performed at 25°C in cylindrical glass tubes with a sample height of 50 mm. The scanning was performed at intervals of 10 min for 24 h.

The typical transmission and backscattering profiles of AgPs in the electrolytic bath, without surfactant CPB, are shown in Figure 1. The transmission profile (Figure 1a) shows a rapid increase in the transmittance signal from the first scans and remains stable in the 1-50 mm range. The transmittance signal increased with time, behavior that is indicative of the formation of a clarifying zone in this region (Figure 1b). Additionally, the backscattering profile (Figure 1c) shows an increase of the backscattering signals as a function of time, characteristic of an increase in particle size from 60 nm to 0.563 µm as was evaluated using the same equipment. This behavior is related to a phenomenon called differential sedimentation [21]. These results revealed that unstable suspensions of AgP were obtained when a surfactant was not used.

Figure 2 shows the typical transmission and backscattering profiles of AgPs in the electrolytic bath with the surfactant CPB. The transmission profile (Figure 2a) shows increases with time throughout the length of the vial. This increase is more pronounced in the region from 18 to 50 mm, which indicates the formation of a clarifying zone in this region. Furthermore, in the region from 0 to 48 mm, the transmission signals are less than 10% during the first 13 h of the experiment, indicating that the solution is opaque in this range. The backscattering profile (Figure 2c) shows a decrease in the signals as a function of time, which is characteristic of a phenomenon called differential sedimentation [21]. The above results revealed that stable suspensions (less than 10% transmission during the first 13 h) of AgP were obtained when CPB was used as a surfactant.

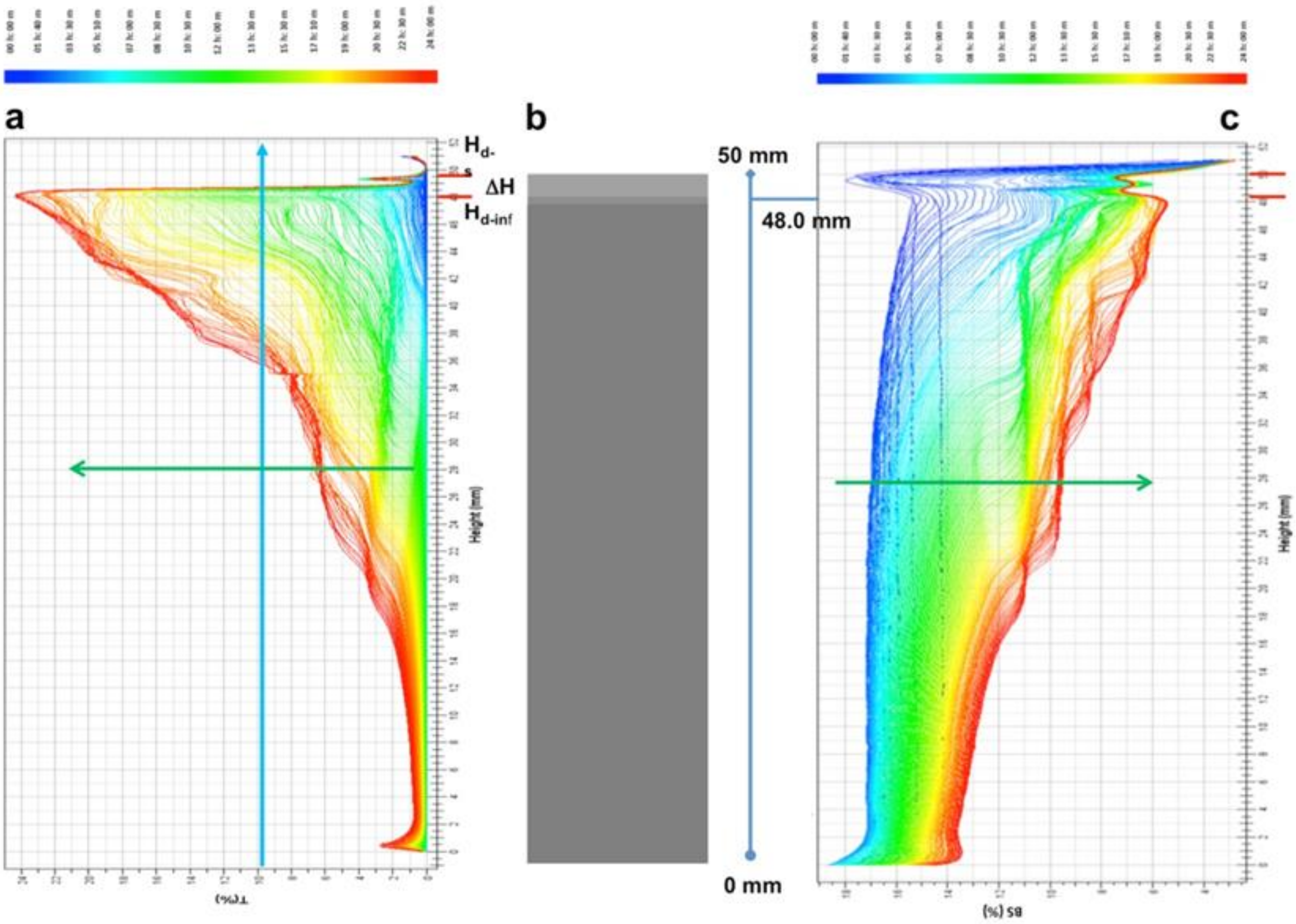


Figure 2 Chemical structure of compound A (a) Transmission and (c) backscattering profiles typical of an electrolytic bath of Cr with silver particles (AgPs) and 5 mM CPB. The data are reported as a function of time (0 to 24 h) and sample height (0 to 50 mm).

Figure 3 shows that the values of the thickness of the clarifying layer (ΔH) in the upper portion of the aqueous AgPs suspension decreased significantly in the presence of the dispersant and increased over time. The best results were obtained for the highest concentrations of CPB. During the time period from 0 to 13 h, the ΔH value of the aqueous AgP suspensions with both 5 and 10 mM CPB was only 0.85 mm, whereas for the suspension without surfactant, ΔH was 48 mm, beginning in the first minutes of the experiment. After 20 h, the ΔH value of the aqueous AgP suspension with 5 mM CPB was only 6.92 mm.

The greater stability of the AgP in the suspension with the dispersant is attributed to the modification of the solid surfaces of the silver particles via the adsorption of CPB. Because of its spatial structure and hydrophilic functional groups, CPB can enhance the electrostatic repulsion and steric hindrance between Ag particles.

Z-Potential measurement

Z-potential measurements were performed on solutions that contained the following: 107 g L^{-1} $CrCl_2 \cdot 6H_2O$ + 23 g L^{-1} NaCl + 50 g L^{-1} H_3BO_3 + 24 g L^{-1} HCOONa + 21 g L^{-1} NH_4Cl + 0.0625 g of AgPs + x (x= 0, 0.1, 0.5, 2.0, 5.0, 10) mM CPB. The concentrations were selected in the range of lower and higher concentrations than the critical micelle concentration (c.m.c.) of CPB in high ionic strength aqueous solutions (c.m.c. ~ 1 mM) [18, 19]. **Figure 4** shows the variation in the Z-potential values of the AgP in the electrolytic baths with different CPB concentrations. First, the Z-potential increased with increasing concentration of the surfactant CPB. As the concentration increased above 5 mM, the Z-potential of the particle became stable, possibly due to the saturated adsorption of CPB on the surface of the AgP. By comparing the results obtained from the stability study and taking into account the Z-potential values obtained in the same solutions, it is clear that the higher Z-potential values correspond to the most stable solutions, which contain higher concentrations of the surfactant CPB; this behavior is associated with the adsorption of the surfactant onto the Ag particle surfaces.

Raman CPB/AgPs analysis

To understand the phenomena related to the adsorption of CPB onto the AgPs, the Raman signature of the AgPs in a Cr electrolytic bath was first studied. In the Raman spectrum of the electrolytic bath containing AgPs in the wavenumber range between 0 and 1300 cm^{-1} (**Figure 5**), the only features present are two well-defined peaks at 54 and 257 nm, associated with the presence of AgPs [22].

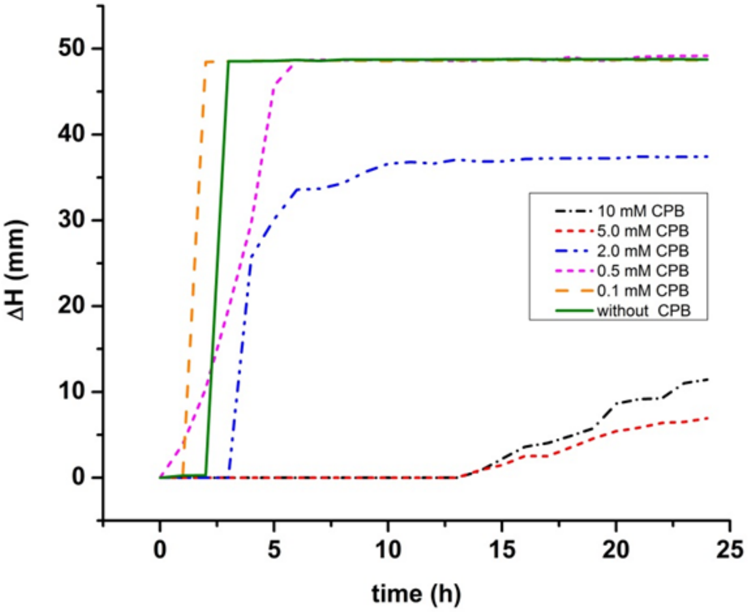


Figure 3 Effect of CPB dosage on the clarifying-layer thickness (ΔH) as a function of time (0 to 24 h).

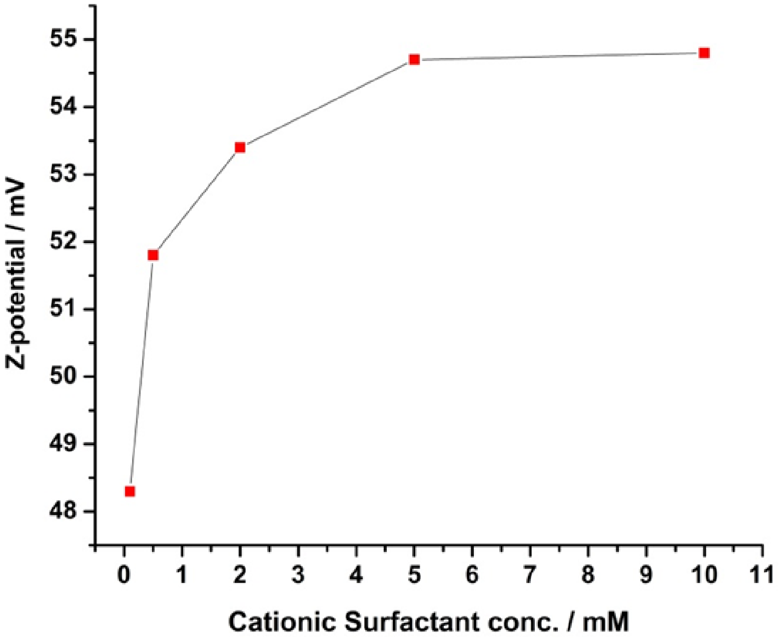


Figure 4 Effects of the cationic surfactant cetylpyridinium bromide (CPB) on the Z-potential of Ag particles in an electrolytic bath of Cr.

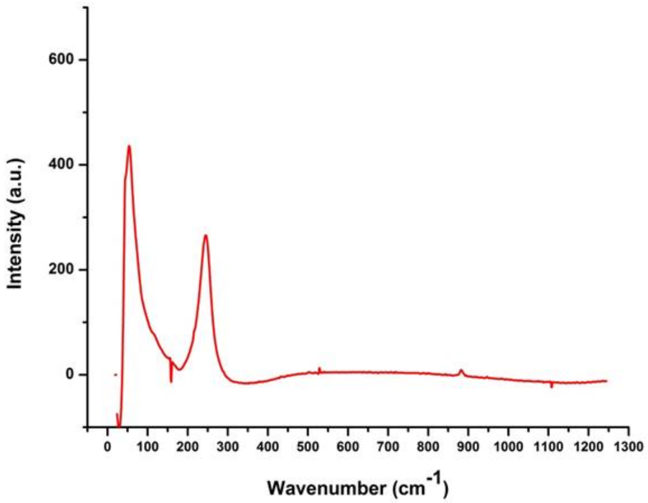


Figure 5 Raman spectra of Ag particles in an electrolytic bath of Cr.

Figure 6 shows the Raman spectra of the electrolytic baths containing a fixed concentration of AgPs and varied concentrations of CPB. The presence of the surfactant produced an additional peak at 1025 cm^{-1}, the relative intensity of which increased with increasing surfactant concentration. This vibrational mode is similar to that reported by Koglin et al. [23] in a theoretical study using density functional theory (DFT) on the adsorption of cetylpyridinium bromide at silver surfaces, and it corresponds to the ring-breathing mode of the pyridinium head group.

On the other hand, the peak located at 244 cm^{-1}, associated with the presence of AgPs, decreased with increasing CPB concentration. At 0.5 mM of CPB, the peak almost disappeared, indicating that at this concentration, the AgPs were completely coated by CPB molecules, inhibiting the photo-interaction of the laser with the Ag nanoparticles. Finally, a third peak at approximately 166 cm^{-1} appeared with the presence of the surfactant, which corresponds at the Ag/Br^{-} Raman interfacial band [23]. The intensity of this peak increased with increasing CPB concentration, which suggests a direct interaction of the AgPs and the surfactant. The results above make it possible to hypothesize that the adsorbed bromide ion acts as a bridge for the surfactant adsorption onto the surface.

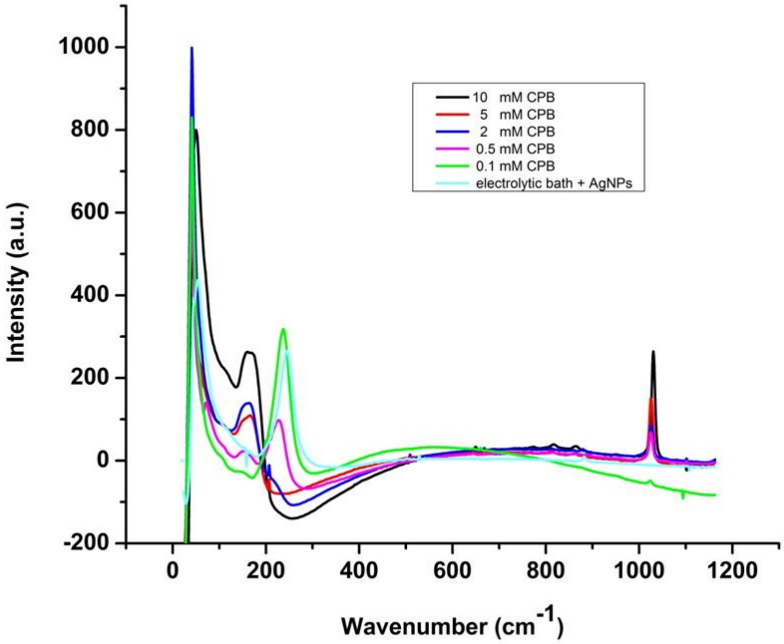


Figure 6 Raman spectra of Ag particles interacting with the surfactant CPB in an electrolytic bath of Cr.

The Raman signals of the cationic CPB surfactant head group (-$N^+C_5H_5$, pyridinium ring) on the silver surface and the intense Ag/Br^- Raman interfacial band suggest that the strong adsorption process is a result of the formation of a pyridinium/bromide/surface system. In accordance with these results, **Figure 7** presents an adsorption model for CPB onto the AgP.

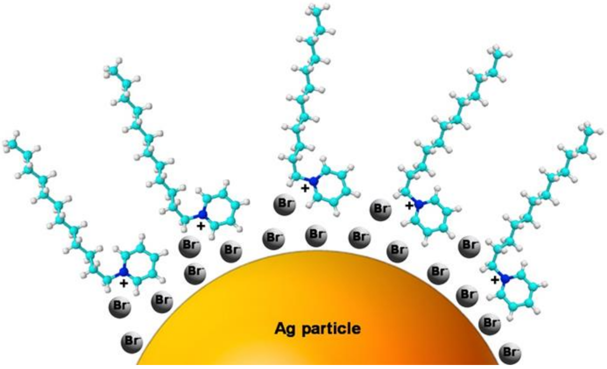


Figure 7 Schematic model of the adsorption of CPB onto Ag surfaces.

Conclusions

The interaction between the cationic surfactant cetylpyridinium bromide (CPB) and silver particles (AgPs) was studied. The *results obtained showed that the introduction* of the surfactant CPB into the electrolytic bath altered the properties of the AgPs suspensions, with an increase in stability over time. The most important effect occurred at concentrations greater than or equal to 5 mM CPB, for which the addition of CPB induced a considerable increase in the stability of the AgPs suspensions. Furthermore, the Z-potential became increasingly positive with increasing CPB concentration.

The stability of the AgPs suspensions using the surfactant CPB is associated with the adsorption of the cationic surfactant onto the surfaces of the AgPs.

By studying the adsorption behavior of the surfactant CPB onto AgPs using Raman spectroscopy, it was possible to observe a strong interaction between the Br^- anions and the AgPs and the adsorption of the pyridinium ring onto the Ag surface. At concentrations greater than or equal to 5 mM of CPB, the surfactant molecules completely coat the silver particles, and therefore, the stability of the suspensions increases. Stable suspensions over 24 h were obtained under these conditions.

References

[1] Korai, H. *J. Inorg. Mater. Jpn.* 1999, 6, 428-436.
[2] Grier, N., in: *Disinfection, Sterilization and Preservation*, Lea and Febiger, Eds, *Block SS* Philadelphia, USA, 1993, 375-389.
[3] Ahearn, D.G; May, L.L; Gabriel, M.M. *J. Ind. Microbiol.* 1995, 15, 372-376.
[4] Jeon, Hyung-Jun; Yi, Sung-Chui; Oh, Seong-Geun. Biomaterials 2003, 24, 4921-4928.
[5] L. Zhao, H. Wang, K. Huo, L. Cui, W. Zhang, H. Ni, Y. Zhang, Z. Wu, P.K. Chu, Biomaterials 2011, 32, 5706-5716.
[6] Kelly, P.J.; Li, H.; Whitehead, K.A.; Verran, J.; Arnell, R.D.; Iordanova, I. Surf. Coat. Technol. 2009, 204, 1137-1140.
[7] Sondi I.; Salopek-Sondi B.; J. Colloid Interface Sci. 2004, 275, 177-182.
[8] Blaser, S.A.; Scheringer M.; MacLeod, M.; Hungerbühler, K. Sci. Total Environ. 2008, 390, 396-409.
[9] Ju-Nam, Y.; Lead, J.R. Sci. Total Environ. 2008, 400, 396-414.
[10] Menno, L.W.; Leo, H.K. Polymers 2011, 3, 340-366.
[11] Prabhu, S.; Poulose, E. Int. Nano Lett. 2012, 2, 2:32
[12] Batchelor-McAuley, Ch.; Tschulik, K.; Neumann, Ch.C.M.; Laborda, E.; Compton, R.G. Int. J. Electrochem. Sci. 2014, 9, 132-1138.
[13] AshaRani, P.V.; Kah Mun, G. L; Prakash Hande, M.; Valiyaveettil, S. ACSNANO 2009, 3, 279-290.

[14] Nguyen, A.V.; Schulze, H.J. Colloidal Science of Flotation. Marcel Dekker. New York, 2004
[15] Chen, H.; Ravishankar, S.; Farinato, R. Int. J. Miner. Process. 2003, 72, 75-86.
[16] Antonietti, M. Curr. Opin. Coll. Inter. Sci. 2001, 6, 244-248.
[17] John, V.T.; Simmons, B.; McPherson, G.L.; Bose, A. Curr. Opin. Coll. Inter. Sci. 2002, 7, 288-295.
[18] Porte, G.; Appell, J. J. Phys. Chem. 1981, 85. 2511-2519.
[19] Palepu R.; Gharibi H.; Bloor D.M.; Wyn-Jones E. Langmuir 1993, 9, 110-112.
[20] Celia, C.; Trapasso, E.; Cosco,D.; Paolino, D.; Fresta, M. Colloid Surface B. 2009, 72, 155-160.
[21] Bordes, C.; Snabre, P.; Frances, C.; Biscans, B. Power Technol. 2003, 130 (1-3), 331-337.
[22] Valmalette, J.C.; Tan, Z.Q.; Abe, H.; Ohara, S. Scientific Reports 2014, 4, 5238 DOI: 10.1038/srep05238.
[23] Koglin, E.; Tarazona, A.; Kreisig, S.: Schwuger, M.J. Colloid and surface A: Physicochemical and Engineering Aspects 1997, 123-124, 523-542.

© 2015, by the Authors. The articles published from this journal are distributed to the public under "**Creative Commons Attribution License**" (http://creativecommons.org/licenses/by/3.0/). Therefore, upon proper citation of the original work, all the articles can be used without any restriction or can be distributed in any medium in any form.

Publication History

Received	23rd	June	2015
Revised	13th	July	2015
Accepted	18th	July	2015
Online	30th	July	2015