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Quantitative analysis of the relationship between the dispersion stability of mixed-surfactant Ag nanoparticles and their composition

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Understanding the surfactant layer composition and morphology of metal nanoparticles (NPs) with single-molecule surfactants is crucial for controlling the properties of NPs. Previously, we reported that the dispersion stability of Ag NPs could be greatly enhanced by mixing n-alkylcarboxylic acid surfactants with two different chain lengths. In this paper, we continued the previous study by quantitatively analyzing the relationship between the surfactant shell composition and the dispersion stability of mixed-surfactant Ag NPs. We found that the Ag NP dispersion stability was greatly influenced by the molar ratio and the difference in chain lengths of the surfactants. To obtain a superior dispersion stability, the molar ratio of the two surfactants with different chain lengths should be close to 1:1, and the difference in chain lengths should be greater than or equal to four carbon atoms. We also found that the dispersion stability of Ag NPs with a mixed surfactant of palmitic acid (***C16***) and dodecanoic acid (***C12***) is insensitive to the type of solvent used.

1. Introduction

Colloidal nanoparticles (NPs) are of tremendous scientific and technological interest due to their unique size-dependent optical and electronic properties.[1-3] Significant attention has been paid to the application of NPs in electronic and optoelectronic devices, such as printed electronic circuits,[4] field effect transistors,[5] solar cells,[6] and light-emitting diodes.[7] Creating stable NP dispersions in media is the first step towards these technical applications because the dispersion stability not only influences the handling, manipulation, and storage period but also affects the final product performance.

To make a stable dispersion of NPs, selecting an appropriate surfactant is of critical importance. The adsorbed surfactant on the effective area of the particle surfaces creates a barrier (either electrostatic or steric) around each particle to prevent them from coming into direct contact with other particles.[8] Thus, it is reasonable that the nature of the surfactant layer plays an important role in forming a stable NP dispersion. For a stable dispersion of metal NPs with a single-molecule surfactant, such as Au NPs and Ag NPs protected with thiol or carboxylic acid, the thickness, conformational freedom, and binding sites of the surfactant barrier play an important role.

It is generally accepted that the organic layer adsorbed to NPs must be sufficiently thick to prevent NP agglomeration.[9,10] Thick organic adlayers provide a steric barrier that counterbalances the attractive van der Waals forces between NPs. Furthermore, some studies have demonstrated that introducing disorder into the surfactant layer also increases NP dispersion stability.[11-13] Thus, kinked surfactants such as oleic acid have been widely used to increase the dispersion stability of NPs.[11] However, these unsaturated fatty acids may not be suitable for certain harsh conditions due to their potential reactivity and rancidification. Various research groups have also investigated the stability of metal NPs by rationally designing surfactant structures.[14-16] For example, Schulz and co-worker prepared Au NPs with surfactant shells of different monodentate poly(ethylene glycol)-thiol surfactants containing long or short alkylene or phenylene spacers.[14] They found that the Au NPs with surfactants containing long alkylene spacers were far more stable than those with surfactants containing short alkylene or phenylene spacers during the oxidative etching process and therefore exhibited improved dispersion stability. Lee and co-worker examined the effects of a variety of multidentate adsorbates on the stability of Au NPs. They successfully improved the dispersion stability of large Au NPs (~50 nm) by using multidentate alkanethiol and attributed this phenomenon to the multidentate chelating effect.[15] Although the dispersion stability of metal NPs with this designed surfactant is very encouraging, the use of this surfactant might be limited by the complex synthetic procedure.

In 2004, Stellacci and co-workers illustrated that two immiscible thiol surfactants on noble metal NPs can phase-separate into ordered ribbon-like domains of alternating composition.[17] The organization of the immiscible molecules has drastic effects on the interfacial properties of the NPs, including NP assembly and molecular recognition. Recently, the same group investigated the relationship between the structure and solubility of alkylthiol-protected Ag NPs with different chain lengths and found that the Ag NPs with mixed surfactants of different chain lengths had superior dispersion stability compared to those with a single surfactant.[18] This result was attributed to the low energy of surfactant disordering in mixed surfactants, endowing the Ag NPs with increased solubility in organic solvents. However, the optimal solubility of Ag NPs obtained in a 1:1:1 molar ratio of dodecylthiol, octylthiol, and heptylthiol was only 0.27 mg/mL in hexane. It should be mentioned that the size distribution of the Ag NPs in their investigation was relatively broad, and the sizes of the Ag NPs used in the dispersion stability comparison were different. Thus, the quantitative comparison of the dispersion stability with surfactants of different chain lengths was ambiguous.

Previously, we reported an interesting phenomenon for improving the dispersion stability of Ag NPs by simply mixing carboxylic acids with different chain lengths.[19] Ag NPs capped by a mixed surfactant with a molar ratio of ≈ 1:1 were found to show higher dispersion stability. This method is extremely simple and may have various potential applications due to its low cost and availability for diverse carboxylic acid surfactants. However, in our previous paper, we calculated the composition of the mixed surfactant by comparing the difference in the amount of organic shell determined by thermal gravimetric analysis (TGA). This indirect method showed poor reproducibility, and the clear relationship between the surfactant shell composition and the corresponding dispersion stability of Ag NPs was not clearly explained.

In this paper, we quantitatively analyzed the relationship between the surfactant shell composition and the dispersion stability of Ag NPs with mixed surfactants. In addition, the effect of mixed surfactants on the dispersion stability of Ag NPs was clearly revealed by investigating more surfactant pairs.

2. Experimental Section

2.1 Materials and Methods.

$AgNO_3$ (99.9%), toluene (99.5%), triethylamine (98%), hexanoic acid (99%, ***C6***), octanoic acid (98%, ***C8***), decanoic acid (98%, ***C10***), ***C12*** (99%), myristic acid (99%, ***C14***), ***C16*** (95%), stearic acid (95%, ***C18***), arachidic acid (99%, ***C20***), p-bromophenacyl bromide (98%), and 18-crown-6 (99%) were purchased from Aldrich-Sigma and used as received. Ag NP size was determined by transmission electron microscopy (TEM; Tecnai G2 F30 S-Twin). Ag NP dispersion stability was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Varian Vista MPX). The size and size distribution of the Ag NPs were determined from more than 100 particles based on TEM images.

2.2 Preparation of Ag NPs.

Monodisperse Ag NPs with sizes of 6.4 ± 0.7 nm were prepared by the modified method of M. Nakamoto et al.[20] Briefly, $AgNO_3$ (17.0 g) was added into a solution composed of triethylamine (400 mL) and palmitic acid (26.4 g). After l0 min of stirring at room temperature, the solution became a white slurry and was heated to 80°C for 2 h. The synthesized Ag NPs were purified three times by the addition of ethanol (400 mL), centrifuged at 3500 rpm for 5 min, and dried overnight under vacuum (11.7 g, yield = 89%, calculated from the metal content).

2.3 Ligand exchange of Ag NPs.

The initial purified Ag NPs (210 mg) were dissolved in toluene (40 mL) containing mixed surfactants of varying composition (the total concentration of mixed surfactants was 0.1 M) under vortex agitation and sonicated for 10 min at 80°C. The ligand-exchanged Ag NPs were purified four times by the addition of ethanol (60 mL), centrifuged at 3500 rpm for 5 min, and dried overnight under vacuum.

2.4 Ag NP Dispersion Stability Analysis.

Ag NP dispersion stability was determined by measuring the Ag concentration of the upper supernatant with ICP-AES.[21] Specifically, the ligand-exchanged Ag NPs (200 mg) were dispersed in toluene (10 g) under vortex agitation and sonicated for 5 min. The dispersion was allowed to stand undisturbed in the dark. After 24 h, the supernatant (~100 μL, recorded the weight of ~100 uL of supernatant) was collected using a micropipette and dissolved in concentrated HNO_3 (1.0 mL) and diluted to 100 g for ICP-AES analysis.

2.5 Analysis of Surfactant Composition on Ag NPs.

HNO_3 (1.0 mL, 60%) was added dropwise to the ligand-exchanged Ag NPs (100 mg) in a 5 mL flask containing a stir bar, and H_2O (1.0 mL) was then added to the solution and stirred for 5 min. Subsequently, the mixed solution was extracted three times with dichloromethane (3.0 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and evaporated to yield an oily or powder compound.

The derivatization procedure was performed following the alkylation method.[22] Specifically, a sample of the surfactant or mixed surfactants (approximately 18 mg) was dissolved in methanol and neutralized to a phenolphthalein end point via the dropwise addition of KOH/methanol solution. The salts were obtained by removing the solution under nitrogen flow. Excess acetonitrile solution of p-bromophenacyl bromide/18-crown-6 (20:1) was added to the salts to produce a total volume of approximately 7 mL. The measured alkylcarboxylic acid concentration was approximately 10 mM. The solution was stirred at 80°C for 15 min to ready it for chromatographic analysis (chromatogram for the standard fatty acids derivatized with p-bromophenacyl bromide at 254 nm; column, reversed-phase symmetrical C18 (5 μm) 46 x 150 mm; flow rate, 1.0 mL min^{-1}; mobile phase, 90/10 $MeOH/H_2O$).

3. Results and discussion

3.1 Examine the influence of alkyl carboxylic acid chain length on Ag NP dispersion stability.

For a stable dispersion of metal NPs with a single-molecule surfactant, the surfactant layer adsorbed to the NPs must be sufficiently thick to prevent NP agglomeration. To examine the influence of alkyl carboxylic acid chain length on Ag NP dispersion stability, monodisperse Ag NPs were dispersed in a 0.1 M toluene solution of carboxylic acids with different chain lengths: ***C6***, ***C8***, ***C10***, ***C12***, ***C14***, ***C16***, ***C18***, and ***C20*** (Fig. 1 and Fig. S1). The dispersion stabilities of Ag NPs in toluene with the surfactants of different chain lengths are given in Fig. S2. It should be noted that the Ag NPs, which were synthesized from the decomposition of Ag palmitate, are highly uniform in size (6.4 ± 0.7 nm, Fig. S3) and exhibit one of the narrowest size distributions reported for the study of NP surface chemistry.

The monodisperse Ag NPs eliminated the influence of size distribution on dispersion stability.

From the color of the supernatant and the amount of precipitate, it was clear that ***C14*** was the most effective surfactant among the tested carboxylic acids. The dispersion stability decreased when the chain length was shorter than ***C14*** due to the insufficient thickness of the surfactant layer. The dispersion stability also decreased when the chain length exceeded ***C14***. This phenomenon was caused by the loss of conformational freedom of the surfactant layer. The solubilities of ***C14***, ***C16*** and ***C18*** at 20°C are 30.4 g, 8.7 g, and 2.0 g per 100 g toluene, respectively;[23] the decreased solubility indicates that the interaction between carboxylic acids becomes larger compared to the interaction between the carboxylic acid and solvent with increasing alkyl chain length. Thus, the adsorbed surfactant with long chain length packed tightly and lost conformational freedom; consequently, the dispersion stability decreased.

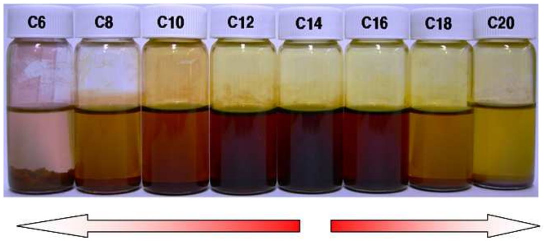

Fig. 1 Photographs of Ag NPs dispersed in 0.1 M toluene solutions of ***C6*** to ***C20***.

3.2 Quantitatively analyze the dispersion stability of Ag NPs with mixed-carboxylate surfactants.

It has been reported that aliphatic acid surfactants adsorbed on the surfaces of Ag NPs can create self-assembled monolayers (SAMs).[24-26] However, the excess free surfactants dissolved in the solution may attach to the SAM and build a multi-layered surfactant on the NPs. To avoid the influence of the free surfactants and study the relationship between the surface chemistry and dispersion stability of Ag NPs, the Ag NPs were ligand exchanged with various carboxylic acids and isolated from the free surfactants in solution using a multi-step separation process. In addition, TEM images demonstrated that the radius of the Ag core did not change after the ligand-exchange reaction (Fig. S4).

The composition of the Ag NP surfactant layer after the ligand-exchange reaction was determined with HPLC. The carboxylic acid surfactants on the Ag NPs were desorbed from the NP surfaces by dissolving the Ag cores with excess HNO_3. The isolated carboxylic acids were quantitatively analyzed using HPLC by tagging the carboxylic acids with strongly UV-absorbing phenacyl groups. This direct method can be used to analyze the compositions of surfactants containing more than two components. Previously, we examined the ratios of mixed surfactants by comparing the amounts of organic surfactants in the Ag NPs using TGA. However, this indirect method showed poor reproducibility due to the following reasons: (i) the small difference between the organic shells before and after the ligand-exchange reaction resulting in unwanted error; (ii) the equation for the calculation of surfactant composition was proposed assuming that the adsorption densities of the surfactants were the same for carboxylic acids of for various chain lengths; and (iii) the equation is suitable for two components, but not for calculating the ratio of mixed surfactants with more than two components.

In our previous paper, we studied the effect of mixed surfactants on Ag NP dispersion stability by comparing the relative absorbances at 420 nm in UV-vis spectra. To quantitatively analyze the dispersion stability of Ag NPs with mixed-carboxylate surfactants, the ligand-exchanged Ag NPs with various carboxylic acids were re-dispersed in toluene and left undisturbed in the dark for 24 h. The amount of Ag NPs in the supernatant was then determined directly by ICP-AES.

Fig. 2a shows the relationship between the dispersion stabilities of Ag NPs ligand exchanged with 1:1 molar ratios of ***C14/Cn*** (n = 6, 8, 10, 12) and the molar ratio of the shorter carboxylic acid chain (***Cn***). The amount of adsorbed surfactant was shown to increase with increasing carboxylic acid chain length (Fig. 2a, red circles). For example, when the Ag NPs were ligand-exchanged with a 1:1 feed ratio of ***C14:C6***, only 15% of ***C6*** was adsorbed. However, in the case of ***C14/C12***, the molar ratio of ***C12*** reached approximately 55% although the feed ratio was the same as for ***C14/C6***. This phenomenon was agreement with the results of our last paper, which indicated that a longer carboxylic acid will adsorb predominantly on the surfaces of Ag NPs. Whitesides et al. also reported that mixtures of n-alkanethiols with different chain lengths will form SAMs on planar Au surfaces such that the composition is enriched in the longer alkanethiols.[27] To the best of our knowledge, this is the first time that a similar phenomenon has been found for a spherical NP.

In terms of dispersion stability, Ag NPs with mixed surfactants showed greater improvements in dispersion stability compared to Ag NPs with a single-molecule surfactant. In addition, the dispersion stability increased with increasing chain length and molar ratio of ***Cn***. For example, only 1.5 mg/g of Ag NPs could be dispersed when the initial surfactant was exchanged with ***C14*** (Fig S1). However, in the case of ***C14/C6***, the dispersion stability of Ag NPs with an approximately 15% molar ratio of ***C6*** was improved to 4.2 mg/g. In the case of ***C14/C8*** with a 24% molar ratio of ***C8***, the dispersion stability increased to 8.2 mg/g. For Ag NPs covered by ***C14/C10*** containing approximately 50% ***C10***, a maximum dispersion stability of 13.7 mg/g was achieved. However, the dispersion stability of Ag NPs with ***C14/C12*** was lower than those with ***C14/C10***, although the molar ratio of ***C12*** (55%) was greater than that of ***C10*** (50%).

Similarly, for Ag NPs ligand exchanged with 1:1 molar ratios of ***C18/Cn***, longer carboxylic acid chain lengths also resulted in greater amounts of adsorbed surfactant (Fig. 2b, red circles). The Ag NP dispersion stability increased with increasing ***Cn*** chain length until ***C14***, and then decreased as the difference between the chain lengths was two carbon atoms (Fig. 2b, black squares). The maximum dispersion stability (11.2 mg/g) was obtained using ***C18/C14*** with a ***C14*** molar ratio of 25%.

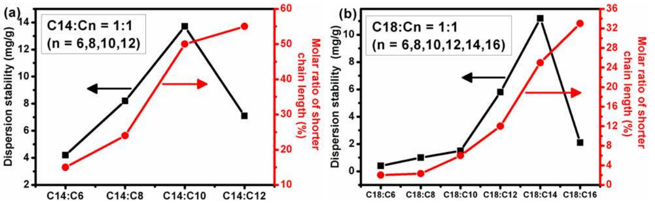

Fig. 2 The relationship between the dispersion stabilities of Ag NPs with (a) ***C14/Cn*** (n = 6, 8, 10, 12) or (b) ***C18/Cn*** (n = 6, 8, 10, 12, 14, 16) and the molar ratio of the shorter carboxylic acid chain (***Cn***).

3.3 Evaluate the exact relationship between dispersion stability and surfactant composition.

Notably, the HPLC analysis detected a small amount of ***C16*** (Table S1) originated from the initial surfactant of the Ag NPs synthesized from the decomposition of Ag(I) palmitate. ***C16*** competed with the added mixed surfactants, and a small amount of ***C16*** remained on the Ag NP surfaces after the ligand-exchange reaction. In contrast to the TGA method employed in our previous paper, the modified HPLC method was able to successfully quantitatively determined the amount of the third carboxylic acid on the Ag NPs. Due to the similar ***C16*** contents on all Ag NP surfaces after the ligand-exchange reaction and the small amount of ***C16***, the effect of remaining ***C16*** on the comparison of Ag NP dispersion stability can be ignored.

To evaluate the exact relationship between dispersion stability and surfactant composition, it is necessary to ensure that only two types of surfactants were present on the Ag NP surfaces. Thus, the initial Ag NPs with ***C16*** surfactant were ligand-exchanged with the mixed surfactants containing different molar ratios of ***C16*** to ***Cn*** (n = 6, 12, and 14).

Similar to the results of the mixed surfactants of ***C14/Cn*** and ***C18/Cn***, in the case of ***C16/Cn***, the molar ratio of ***Cn*** adsorbed on the Ag NP surfaces increased obviously with increasing ***Cn*** feed ratio and chain length. For example, the molar ratio of ***C6*** adsorbed on Ag NP surfaces increased from 15% to 55% as the feed ratio of ***C6*** increased from 70% to 95% (Fig. 3a, red circles). In the case of ***C16/C12*** (Fig. 3b, red circles), the molar ratio of ***C12*** increased from 10% to 84% as the feed ratio increased from 40% to 95%. Similar adsorption results were observed for ***C16/C14*** (Fig. 3c, red circles). Combining the three adsorption results demonstrated that more surfactants (***Cn***) were adsorbed on the Ag NP surfaces as n increased. For example, when the feed ratio of ***Cn*** was 70%, the molar ratios of ***C6***, ***C12***, and ***C14*** were 15%, 44%, and 53%, respectively, and when the feed ratio of ***Cn*** was 95%, the molar ratios of ***C6***, ***C12***, and ***C14*** were 55%, 84%, and 87%, respectively. These results were consistent with the results for ***C14/Cn*** and ***C18/Cn*** (Figs. 2a and 2b, respectively, red circles).

For dispersion stability, the maximum dispersion stability was obtained when the molar ratio of adsorbed short and long chain carboxylic acids was close to 1:1 (Figs. 3a-c). For example, only 3.0 mg/g of Ag NPs could be dispersed in toluene when they were capped with a 15% molar ratio of ***C6***. When the molar ratio of ***C6*** was in the range of 50~55%, the Ag NP dispersion stability was greatly improved to approximately 10.0 mg/g. In contrast to the dispersion stability of Ag NPs with a 24% molar ratio of ***C6*** (4.0 mg/g), Ag NPs with a similar molar ratio of ***C12*** showed better dispersion stability (9.7 mg/g). The dispersion stability reached the maximum (11.3 mg/g) when the molar ratio of ***C12*** increased to 43% and then decreased as the molar ratio of ***C12*** increased further. Interestingly, in the case of ***C16/C14***, Ag NPs with a ~35% molar ratio of ***C14*** showed lower dispersion stability (6.4 mg/g) than Ag NPs with a ~35% molar ratio of ***C12*** (11.1 mg/g). The trend of dispersion stability for ***C16/C14*** was similar with that of ***C16/C12***; however, its maximum dispersion stability (8.0 mg/g, 52%) was lower than those of ***C16/C6*** (10.4 mg/g, 55%) and ***C16/C12*** (11.2 mg/g, 43%). This phenomenon wherein the dispersion stability decreased when the difference in chains length was two carbon atoms is consistent with the results for ***C18/C16*** and ***C14/C12***.

Based on the above results for ***C16/C6***, ***C16/C12***, and ***C16/C14***, it is clear that to maximize the dispersion stability, the molar ratio of the two types of surfactants should be ≈1:1, and the chain length difference should be greater than or equal to four carbon atoms.

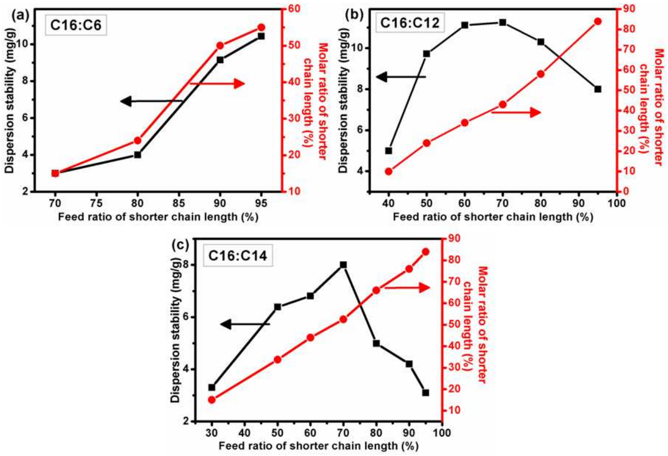

Fig. 3 The relationships between the dispersion stabilities of Ag NPs with (a) ***C16/C6***, (b) ***C16/C12***, or (c) ***C16/C14*** and the molar ratio of the shorter carboxylic acid chain.

3.4 Comparison of the dispersion stabilities of Ag NPs with various surfactants in different solvents.

The dispersion stabilities of Ag NPs with single and mixed surfactants were also compared in different solvents (Fig. 4). In the case of Ag NPs with ***C16***, the dispersion stability decreased by nearly 10 times from 6.2 mg/g to 0.6 mg/g when the solvent was changed from hexane to dodecane. However, the Ag NPs with ***C16/C12*** showed stable dispersion stabilities in the tested solvents; the dispersion stability only decreased by approximately 10% from 16.7 mg/g to 15.0 mg/g as the solvent changed from hexane to dodecane.

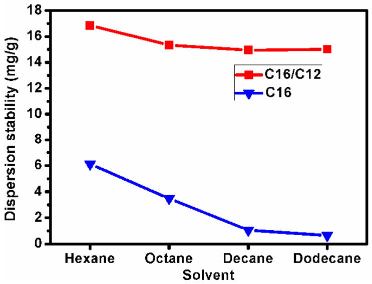

Fig. 4 Comparison of the dispersion stabilities of Ag NPs with various surfactants in solvents ranging from hexane to dodecane.

It is well known that when the interaction between the solvent and NPs is larger than the inter-particle interaction, stable NPs dispersions are obtained. Various research groups have reported that single-molecule surfactants, especially alkylthiols or alkylcarboxlylates, on metal NPs can interdigitate with the surfactants of adjacent NPs.[28,29] For example, Wang and co-workers observed the bundling and interdigitation of thiolate molecules adsorbed on Ag NPs (~5.5 nm) using chemical imaging with an energy-filtered transmission electron microscope.[28] Thus, it is believed that hexane molecules could be interdigitated into the space of the surfactants adsorbed on Ag NP surfaces. The number of interdigitated molecules decreased with increasing size or chain length of the solvent.

This caused the interaction between the solvent and the surfactant to be less significant than inter-particle interaction, leading to NP aggregation. Thus, the dispersion stability of Ag NPs with ***C16*** decreased dramatically as the solvent changed from hexane to dodecane.

In the case Ag NPs protected with mixed surfactant (***C16/C12***), the interdigitation of the surfactant adsorbed on the Ag NPs was disturbed due to the different chain lengths, causing the inter-particle interaction to be less significant than the interaction between Ag NPs with ***C16***. Stellacci et al. reported that the interdigitation of neighboring particles can be impeded by introducing a mixed surfactant of dodecylthiol and octylthiol on Ag NPs.[18] This was attributed to the fact that the last four carbons in the dodecylthiol chain are free to rotate and form gauche conformations, resulting in a lower disordering energy. This idea can also be applied to explain the higher dispersion stability exhibited by Ag NPs with ***C16/C12*** compared to those with ***C16/C14***. Compared with ***C16/C14***, Ag NPs with ***C16/C12*** have weaker inter-particle interactions because the conformational entropy arising from the last two carbons (***C16/C14***) is lower than that of the last four carbons (***C16/C12***). Based on these results, we were able to infer that the low inter-particle interaction arising from the mixed surfactant effect may play a vital role in improving the dispersion stability of Ag NPs.[18]

4. Conclusions

In conclusion, the dispersion stabilities of Ag NPs with mixed surfactants were examined quantitatively. The dispersion stability was greatly improved by the mixed surfactants. To obtain the maximum dispersion stability, the molar ratio of the two types of surfactants should be ≈1:1, and the chain length difference should be greater than or equal to four carbon atoms. In addition, it was found that increasing the chain length of the shorts of the two surfactants increased the amount of surfactant adsorbed during the ligand-exchange reaction. We also found that the dispersion stability of Ag NPs with a mixed surfactant of ***C16*** and ***C12*** is insensitive to the type of solvent used. We believe that this simple and low-cost method for improving the dispersion stability of NPs can be applied in fields that require high solid contents of Ag NPs with single-molecule surfactants, such as Ag nano-ink for printable electronics. An investigation of the detailed mechanism for the mixed-surfactant effect using theoretical modeling and computer simulation is now in progress.

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Notes and references

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