

# Semi-quantitative determination of cationic surfactants in aqueous solutions using gold nanoparticles as reporter probes

Chi-Lap Kuong · Wei-Yu Chen · Yu-Chie Chen

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**Abstract** Concentrations of cationic surfactants in aqueous solutions have been estimated on the basis of changes in the color of gold nanoparticles, used as reporter probes. We have shown that the colors of gold nanoparticles with anionic protective groups on their surfaces shift from red to indigo/purple and then back to red in a range of cationic surfactant solutions in which concentrations vary from very low to above the theoretical CMCs. The color changes occur near the theoretical CMCs, presumably because the presence of surfactant micelles in the solution prevents the gold nanoparticles from aggregating. We have used gold nanoparticles as reporter probes to determine the concentrations of cationic surfactants in products such as hair conditioners, which often contain large amounts of alkyl-trimethylammonium halides. Although this approach can only provide an estimate, it can be performed simply by addition of a given amount of gold nanoparticles to a series of diluted solutions, without the need for instruments or labor-intensive procedures.

**Keywords** Gold nanoparticles · Cationic surfactants · Iron oxide particles · Chemical sensor · SALDI MS

## Introduction

Gold nanoparticles have been widely used as sensing probes for different types of analyte, including ions [1–5], gases [6, 7], and biomolecules [8–13]. They can be chemically modified to enable recognition of specific targets. Recognition may result in aggregation of gold nanoparticles and a consequent color change of the solution, usually taken as evidence of the presence of the target species. Excess ions present in a gold nanoparticle suspension can also cause aggregation and fusion of gold nanoparticles. A red shift of the wavelength of the maximum absorption band of the suspension is commonly observed.

Conventionally, the critical micelle concentration (CMC) of surfactants is determined by light scattering [14], surface tension [14], and spectroscopy [15, 16]. When spectroscopy is used, organic dyes are usually added to the surfactant solution to indicate the CMC point on the basis of the abrupt change of the absorption spectra of the dyes [15, 16]. Because gold nanoparticles have visible colors, they can potentially be used as reporter probes for determination of the CMCs of surfactants. Gold nanoparticles with anionic protection groups on their surfaces tend to aggregate with a color shift from red to indigo or purple if excess cations, for example cationic surfactants, are present in solution. The presence of cations in the solution results in uneven charge distribution on their surfaces, which may cause further aggregation as a result of electrostatic interaction. We suspect that the presence of surfactant micelles in the solution might prevent aggregation of the nanoparticles. Thus, as the concentration of surfactants approaches their CMC in a gold nanoparticle suspension, the color might remain red. It is of interest whether or not the color of a surfactant solution containing gold nanoparticles will remain

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C.-L. Kuong · W.-Y. Chen · Y.-C. Chen (✉)  
Department of Applied Chemistry,  
National Chiao Tung University,  
Hsinchu 300, Taiwan  
e-mail: yuchie@mail.nctu.edu.tw

Y.-C. Chen  
Institute of Molecular Science, National Chiao Tung University,  
Hsinchu 300, Taiwan

red around its CMC. We have proposed a mechanism that results in changes in the color of gold nanoparticles in a cationic surfactant solution (Scheme 1). When the concentration of cationic surfactants is far below their CMC, free cationic surfactant molecules may become attached to the surfaces of negatively charged gold nanoparticles. The gold nanoparticles in the solution then have uneven charge distribution on their surfaces, which results in aggregation of the nanoparticles, owing to electrostatic interactions. The color of gold nanoparticles then shift from red to indigo. As the concentration of the cationic surfactants is further increased, surfactant micelles and free surfactant molecules are present in the sample solution simultaneously. Some of the gold nanoparticles become attached to the surfaces of the surfactant micelles. The color of the gold nanoparticles remains red. Free cationic surfactant molecules bind to the surfaces of the gold nanoparticles and cause uneven charge distribution on the surfaces of the nanoparticles, however. Further aggregation of gold nanoparticles occurs as a result of electrostatic interactions. The mixing of red and indigo gold nanoparticles results in the sample solution becoming purple. As the concentration of the cationic surfactant approaches the CMC, surfactant micelles dominate the solution and the color of the sample solution remains red. Negatively charged gold nanoparticles, on the other hand, attract neither anionic nor nonionic surfactants, so the color would remain unchanged in the presence of these types of surfactant. We have investigated the color changes for several surfactant solutions, including alkyltrimethylammonium halides, sodium dodecyl sulfate (SDS), and Tween 20, with added gold nanoparticles.

Alkyltrimethylammonium halides are among the common ingredients present in such consumer products as softeners, bactericides, antistatics, and hair conditioners. Capillary electrophoresis [17–19], gas chromatography–mass spectrometry [20], fast atom bombardment (FAB) mass spectrometry [21], and ion-spray mass spectrometry [21] have been used to determine alkyltrimethylammonium

surfactants in hair conditioners. As an alternative we are investigating gold nanoparticles as reporter probes for approximate determination of the concentrations of cationic surfactants in a hair conditioner. The concentrations of alkyltrimethylammonium halides in hair conditioner can be estimated on the basis of the color changes of a series of diluted hair-conditioner solutions on addition of an appropriate amount of gold nanoparticles.

## Experimental

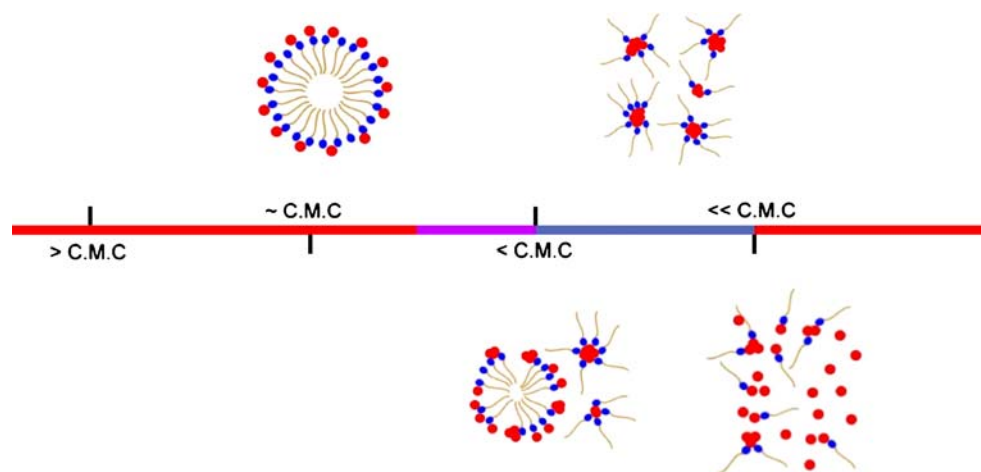
### Reagents

Hexadecyltrimethylammoniumbromide (C16+), trisodium citrate, iron(III) chloride hexahydrate, ammonium hydrogen carbonate, and sodium sulfite were obtained from Riedel-de Haën (Seelze, Germany). Aqueous ammonia, octadecyltrimethylammonium bromide (C18+), tetradecyltrimethylammonium bromide (C14+), dodecyltrimethylammonium bromide (C12+), decyltrimethylammonium bromide (C10+), and tetraethoxysilane (TEOS) were obtained from Fluka (Buchs, Switzerland). Tetrachloroaurate and ethanol were obtained from Showa (Tokyo, Japan), and dimethylformamide (DMF) and sodium dodecyl sulfate (SDS) were obtained from J.T. Baker (Phillipsburg, NJ, USA). Tween 20, citric acid, and 3-aminopropyl triethoxysilane (APTES) were purchased from Sigma (St Louis, MO, USA). Hydrochloric acid was obtained from Merck (Seelze, Germany), and succinic anhydride was obtained from Aldrich (Milwaukee, WI, USA). Hair conditioner was purchased from a local grocery store.

### Preparation of gold nanoparticles

Gold nanoparticles were prepared using Frens' method [22]. An aqueous tetrachloroaurate solution ( $0.1 \text{ mg mL}^{-1}$ ,

**Scheme 1** Proposed mechanism of the color changes of gold nanoparticles in a cationic surfactant solution



50 mL) was heated to boiling and trisodium citrate (1%, 1 mL) was added with stirring. The color change of the solution from indigo to brilliant red indicated the formation of monodisperse spherical particles [22]. By examination of a TEM image 500 gold nanoparticles were counted; the average particle diameter ( $23.3 \pm 3.2$  nm) was determined by use of SigmaScan Pro5 (Systat Software).

#### Preparation of surfactant solutions

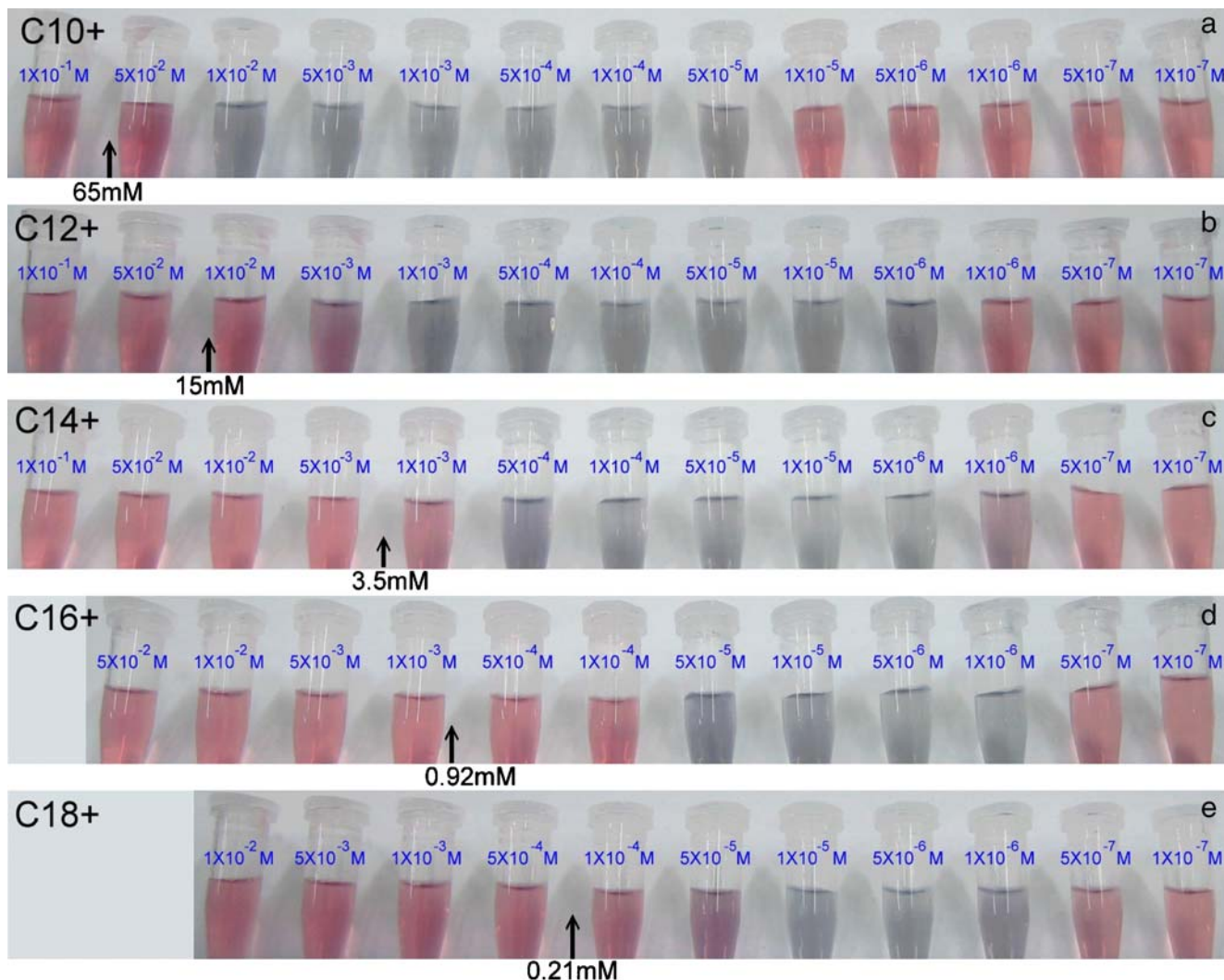
Stock solutions of alkyltrimethylammonium bromide surfactant (C10+, C12+, C14+, C16+, and C18+), SDS, and Tween 20 were prepared in deionized water. Working concentrations were prepared from these by serial dilution with deionized water. Samples of hair conditioner were prepared by serial dilution with deionized water then sonication in hot water.

#### Using gold nanoparticles as reporter probes

The gold nanoparticle solution (0.45 mL) obtained as described above was added to the surfactant solutions (0.45 mL) at different concentrations. After leaving the mixture to stand at ambient temperature for 10 min, the color change of the samples was recorded by use of a camera and analyzed by UV–visible absorption spectrophotometry.

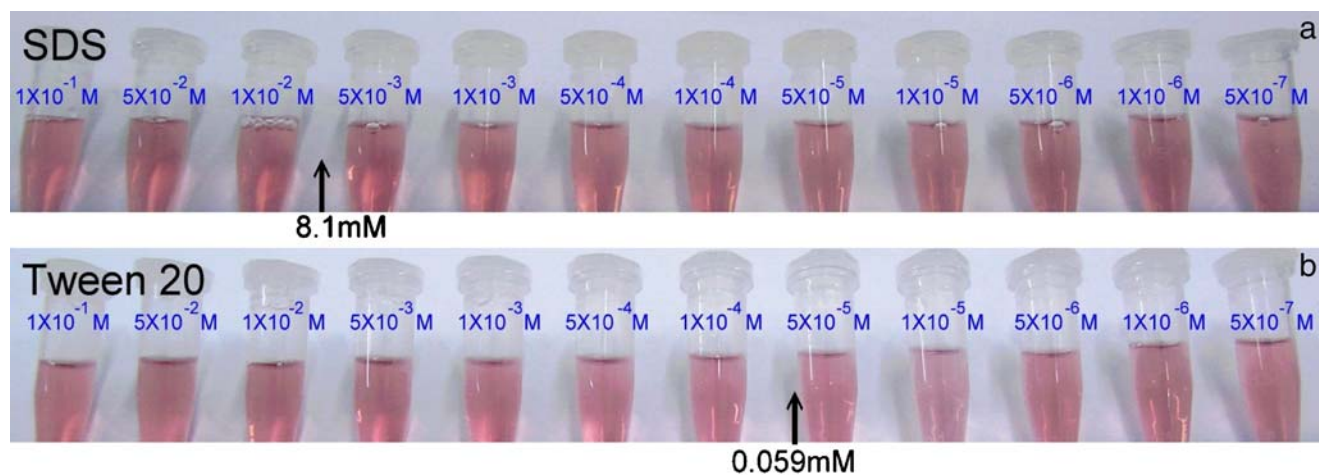
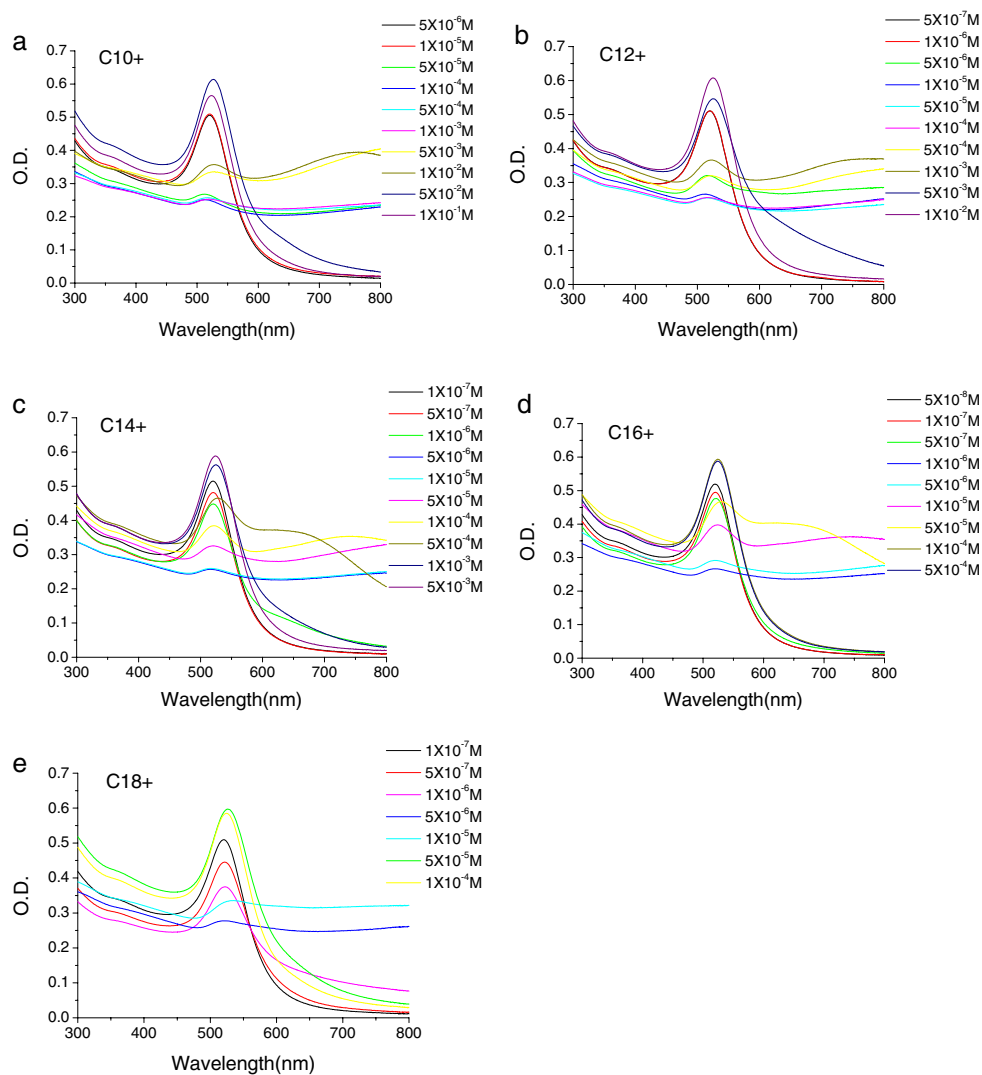
#### Fe<sub>3</sub>O<sub>4</sub>–SALDI MS analysis

Iron oxide nanoparticles were prepared on the basis of the procedures reported by Cao et al. [23]. Sample preparation for Fe<sub>3</sub>O<sub>4</sub>–SALDI MS analysis has been described elsewhere [24]. The particle suspension (0.2 μL) was deposited on to a sample plate followed by deposition of the analyte solution (0.2 μL). After evaporation of the solution the sample was ready for Fe<sub>3</sub>O<sub>4</sub>–SALDI-MS analysis.



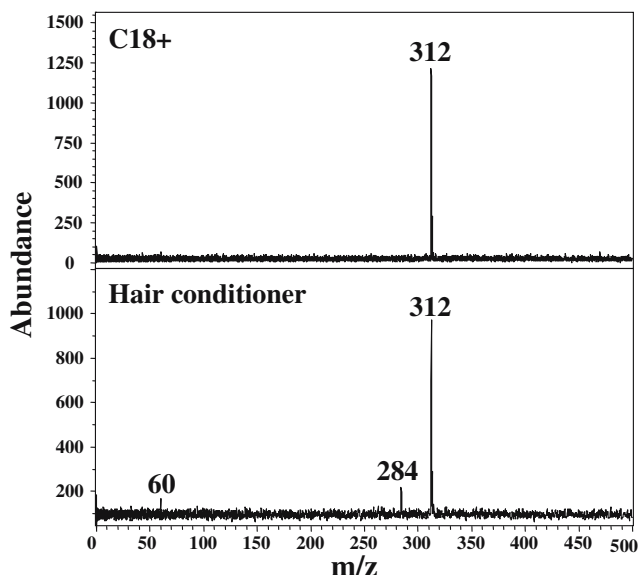
**Fig. 1** Photographs of a series of diluted surfactant solutions: (a) C10+, (b) C12+, (c) C14+, (d) C16+, and (e) C18+ with added gold nanoparticles. The theoretical CMC point locates as the arrow bar indicates

**Fig. 2** Absorption spectra of a series diluted surfactant solutions: (a) C10+, (b) C12+, (c) C14+, (d) C16+, and (e) C18+ with added gold nanoparticles



**Fig. 3** Photographs of a series of diluted surfactant solutions: (a) SDS and (b) Tween 20 with added gold nanoparticles. The theoretic CMC point locates as the arrow bar indicates

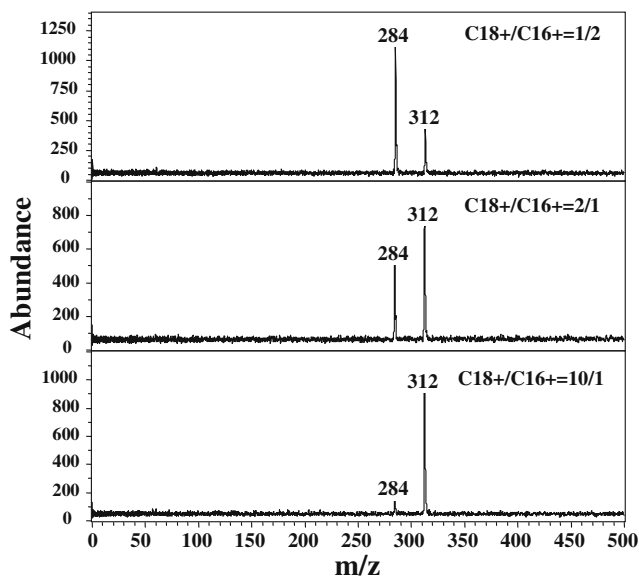




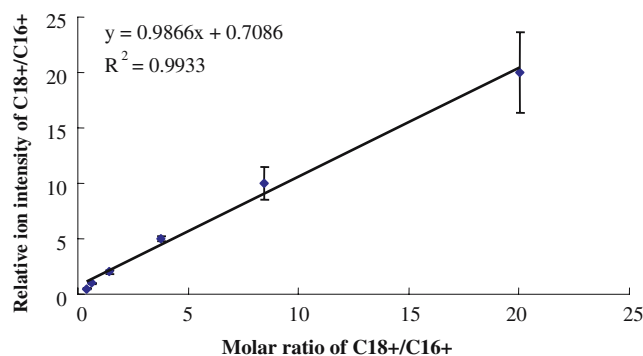
**Fig. 4**  $\text{Fe}_3\text{O}_4$ -SALDI mass spectra of (a) C18+ ( $0.1 \text{ mg mL}^{-1}$ ,  $0.2 \text{ }\mu\text{L}$ ) and (b) a diluted hair conditioner ( $0.5 \text{ mg mL}^{-1}$ ,  $0.2 \text{ }\mu\text{L}$ )

#### Instrumentation

All absorption spectra were obtained by use of a Varian Cary 50 absorption spectrophotometer (Melbourne, Australia). All mass spectra were obtained by use of a Bruker Daltonics Biflex III time-of-flight mass spectrometer (Leipzig, Germany). The mass spectrometer was equipped with a 337-nm nitrogen laser, a 1.25-m flight tube, and a sample target with the capacity to load 384 samples simultaneously. The accelerating voltage was 19 kV.



**Fig. 5**  $\text{Fe}_3\text{O}_4$ -SALDI mass spectra of the mixtures of C18+/C16+ with the molar ratios of (a) 1/2, (b) 2/1, and (c) 10/1



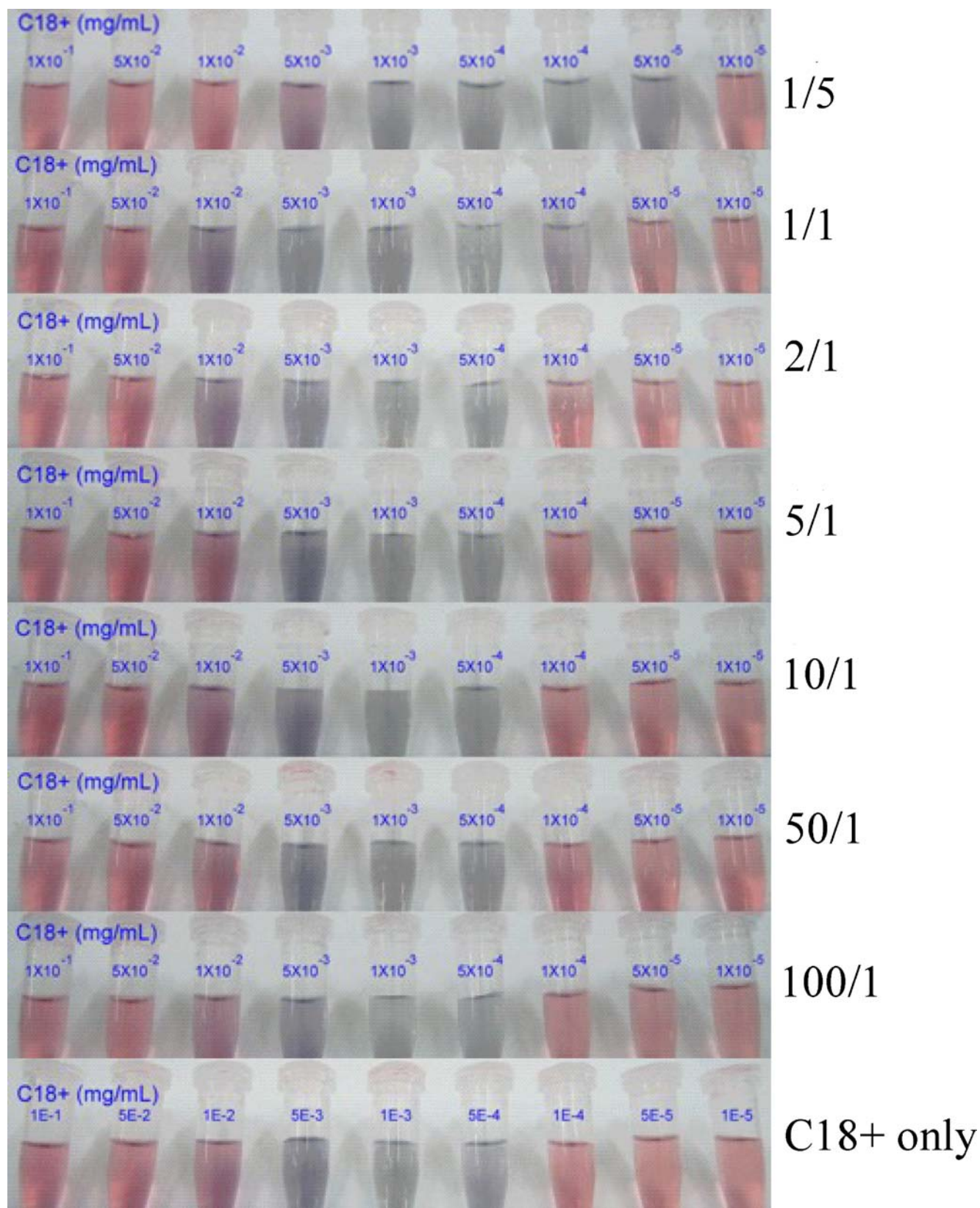
**Fig. 6** The relative ion intensity of C18+/C16+ in  $\text{Fe}_3\text{O}_4$ -SALDI mass spectra as a function of the molar ratio of C18+/C16+

#### Results and discussion

Photographs of different concentrations of alkyltrimethylammonium (C10+, C12+, C14+, C16+, and C18+) surfactant solutions with added gold nanoparticles are shown in Fig. 1a–e. As expected, the colors of the surfactant solutions changed from red to indigo and then back to red as concentrations were increased beyond the CMCs. An arrow in each photograph indicates the theoretical CMC for each surfactant. The color change from indigo/purple to red always occurs at a concentration which is a factor of 5–10 lower than the theoretical CMC for each surfactant [25]. It is also apparent the number of vials containing a series of diluted samples with colors other than red decreases with increasing carbon-chain length of the alkyltrimethyl cationic surfactants.

Figure 2a–e show the absorption spectra of the C10+, C12+, C14+, C16+, and C18+ solutions ( $0.45 \text{ mL}$ ), respectively, over a range of concentrations spanning their CMCs with added gold nanoparticles ( $0.45 \text{ mL}$ ). These results correspond to those in Fig. 1. The absorption bands at  $\sim 520 \text{ nm}$  in Fig. 2 gradually decrease as the surfactant concentration increases from far below the CMC to near the CMC. A second broad band starts to appear at approximately  $700 \text{ nm}$ . This band is responsible for the indigo color and is because of aggregation of the gold nanoparticles with increasing surfactant concentration. As the surfactant concentration reaches a factor of 5–10 less than the theoretical CMC, the maximum absorption band shifts back to the original wavelength ( $\sim 520 \text{ nm}$ ) and the second band vanishes. The CMC for each surfactant always appears above the concentration of the color changes from indigo and back to red.

With anionic surfactants and nonionic surfactants in the presence of gold nanoparticles no color change occurs among the series of sample solutions over a range of concentrations including the theoretical CMC. Photographs of SDS solutions at different concentrations with added gold nanoparticles are shown in Fig. 3a. The theoretical



**Fig. 7** Photographs of a series of the mixtures of C18+/C16+ with the relative weight ratios of (a) 1/5 (b) 1/1 (c) 2/1 (d) 4/1 (e) 10/1 (f) 50/1 (g) 100/1 and (h) C18+ only; with added gold nanoparticles

CMC point is indicated by an arrow. Presumably, gold nanoparticles with negatively charged functionality tend to repel anionic surfactants. Similarly, with nonionic surfactants, e.g. Tween 20, no color changes are observed over a concentration range including the theoretical CMC (Fig. 3b). It follows that gold nanoparticles with negatively charged functionality on their surfaces can be used as reporter probes for cationic surfactants only.

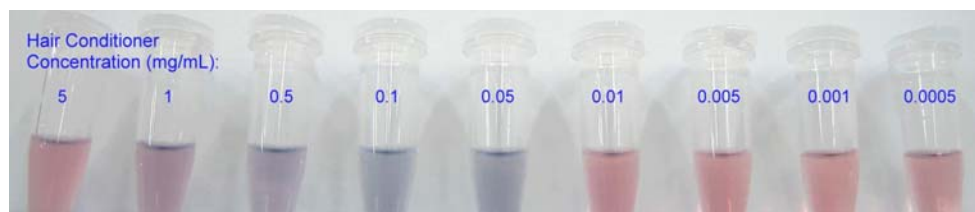
Because anionic and nonionic surfactants do not interact with the negative nanoparticles to give color changes, it seemed possible that we could use the gold nanoparticles to estimate the concentration of cationic surfactants. Because alkyltrimethylammonium halide is a major surfactant in hair conditioners, we demonstrated the feasibility of using gold nanoparticles as the reporter in the semi-quantitative determination of alkyltrimethylammonium cations in these products. Because determination of the concentration of cationic surfactants in a real sample relies on comparison of the color changes with those of standard surfactant solutions at a series concentrations, it is necessary to know which cationic surfactants are the major components of the hair conditioner. Although the factory claimed that C18+ is one of the major cationic surfactants in the hair conditioner, we confirmed the presence of alkyltrimethylammonium surfactants in the sample by use of  $\text{Fe}_3\text{O}_4$ -SALDI MS, which is suitable for analysis of small analytes because of its low matrix background [24], to examine the presence of alkyltrimethylammonium surfactants in the sample. Only one peak appears in the  $\text{Fe}_3\text{O}_4$ -SALDI mass spectrum of C18+ standard solution ( $0.1 \text{ mg mL}^{-1}$ ,  $0.2 \mu\text{L}$ ) shown in Fig. 4a. The peak appearing at  $m/z$  312 is generated from C18+ by loss of its counter anion. Figure 4b also shows the  $\text{Fe}_3\text{O}_4$ -SALDI mass spectrum of the diluted hair conditioner ( $0.5 \text{ mg mL}^{-1}$ ,  $0.2 \mu\text{L}$ ), using iron oxide particles as the SALDI matrix. The peak at  $m/z$  312 dominates the mass spectrum. Presumably, the peak at  $m/z$  60 is a fragment derived from C18+, i.e.  $\text{NH}(\text{CH}_3)_3^+$ . The ion peak can be observed if the laser power is high enough. Because C18+ is the major component of the hair conditioner and it is a pre-charged ion, it is not surprising that this C18+ peak seems to be the base peak in the mass spectrum. The presence of C18+ ions may easily suppress the ions generated from other ingredients in the hair conditioner. The peak at  $m/z$  284 is presumably derived from C16+ by loss of its counter anion.

To estimate the relative amounts of C18+ and C16+ in the hair conditioner, a series of solutions containing different proportions of C18+/C16+ were examined. Figure 5a–c show the  $\text{Fe}_3\text{O}_4$ -SALDI mass spectra of mixtures of C18+ and C16+ in the molar ratios 1:2, 2:1, and 10:1. Only two peaks at  $m/z$  284 and 312, and no other background ions, appear in the mass spectrum, resulting in an interference-free background beneficial for quantitative analysis. We generated a calibration curve by plotting the relative ion intensity, C18+/C16+, as a function of the molar ratio of C18+/C16+ (Fig. 6). From the results in Figs. 4b and 6 we estimated the molar ratio of C18+/C16+ in the hair conditioner to be 7.0/1.0.

Because the real sample contains two cationic surfactants, we prepared a series of standard solutions containing C18+/C16+ in different ratios to investigate the color changes on addition of gold nanoparticles. Photographs of the sample solutions containing C18+ and C16+ in the weight ratios 1/5, 1/1, 2/1, 5/1, 10/1, 50/1, and 100/1 (marked on the left side), which correspond to molar ratios of 0.19/1, 0.93/1, 1.86/1, 4.64/1, 9.28/1, 46.6/1, and 92.8/1, respectively, are shown in Fig. 7a–g. The concentration of C18+ in each figure is marked on the top of each vial in Fig. 7 and the concentration of C16+ was varied so the ratio to C18+ varied as stated above. In Fig. 7a, it is obvious that the samples in the fourth to the eighth vials counted from the left contain C18+/C16+ at the concentrations  $5 \times 10^{-3} \text{ mg mL}^{-1}/2.5 \times 10^{-2} \text{ mg mL}^{-1}$ ,  $10^{-3} \text{ mg mL}^{-1}/5 \times 10^{-3} \text{ mg mL}^{-1}$ ,  $5 \times 10^{-4} \text{ mg mL}^{-1}/2.5 \times 10^{-3} \text{ mg mL}^{-1}$ ,  $10^{-4} \text{ mg mL}^{-1}/5 \times 10^{-4} \text{ mg mL}^{-1}$ , and  $5 \times 10^{-5} \text{ mg mL}^{-1}/2.5 \times 10^{-4} \text{ mg mL}^{-1}$ , respectively, have colors other than red. In Fig. 7b, there are still five samples with color changes. As the relative weight ratio of C18+/C16+ increases to >2/1, only four samples have color changes (Fig. 7c–g). When the concentration of C18+ is much higher than that of C16+, the pattern of the color changes resembles that containing only C18+ as shown in Fig. 7h. Furthermore, as the relative ratio of C18+/C16+ is increased to >5/1, the color in the sample in the second vial counting from the left side changes to deep red. We can therefore use the color changes to estimate the possible relative ratio of C18+/C16+.

Figure 8 shows the photographs obtained from hair conditioner solutions serially diluted with deionized water with added gold nanoparticles. It is apparent that four

**Fig. 8** Photographs of a series diluted hair conditioner solutions with the addition of gold nanoparticles





samples have colors other than red starting from the second sample to the fifth counting from the left. Furthermore, the sample in the second vial has a color near deep red. On the basis of the color changes in Fig. 7, the relative concentration of C18+/C16+ is estimated to be  $>2/1$ , which was also shown previously using  $\text{Fe}_3\text{O}_4$ -SALDI for characterization in Fig. 4b. The concentration of C18+ present in the hair conditioner is estimated to be 1% by comparison of the photographs presented in Figs. 7 and 8. Hair conditioners usually contain 0.5–2% alkyltrimethyl surfactants. The factory claimed the major ingredients of the hair conditioner included stearyl alcohol, dimethicone, amodimethicone, glycerin, paraffin, cetyl palmitate, methyparaben, propylparaben, arginine, and citric acid in addition to C18+. These chemicals are either neutral or uncharged in aqueous solution except arginine and citric acid. Arginine might have net positive charges and citric acid might carry net negative charges. As is apparent from Fig. 3, neutral and anionic species have no effect on the color changes of gold nanoparticles. Thus, only positively charged arginine may affect the colors of gold nanoparticles in hair conditioner solutions. We conducted a series of experiments using gold nanoparticles as the reporter probes by spiking mixtures of C18/C16 in the molar ratio 7/1, the molar ratio of C18/C16 present in the hair conditioner samples, with different concentrations of arginine. The patterns of the color changes of the C18/C16 mixtures spiked with concentrations of arginine  $<2 \times 10^{-4} \text{ mol L}^{-1}$  resembled each other (results not shown), i.e. if the concentration of arginine in the sample solution was below  $2 \times 10^{-4} \text{ mol L}^{-1}$  the colors of gold nanoparticles were unaffected by its presence and the pattern of the color changes was similar to that shown in Fig. 8. Thus ingredients other than cationic surfactants in the hair conditioner samples do not affect the color of gold nanoparticles. These results indicate that the concentration of the target cationic surfactant can be determined by adding gold nanoparticles to solutions of the cationic surfactant and comparing the color changes in a series of diluted samples with those from a series of diluted standard solutions. When reporter probes of different diameters and shapes have different colors, the colors of both the standard solutions and samples also vary, so the color of the sample still matches that of the surfactant standard solution with the corresponding concentration. Thus, reproducible results can be obtained using this approach, because standard surfactant solutions should be always prepared for investigation during analysis.

## Conclusions

We have demonstrated that gold nanoparticles can be used as reporter probes for determination of the concentration of

cationic surfactants, for example alkyltrimethylammonium halides, in hair conditioner. The colors of the sample solutions are compared with those of standard surfactant solutions. Because anionic and nonionic surfactants do not cause changes in the color of the gold nanoparticle suspension, the presence of anionic and nonionic surfactants in real samples does not interfere with the assay. No instrumentation or tedious sample pretreatment is required for analysis of real samples. Only a series of dilutions need to be prepared and the analysis can be completed within 10 min. Amounts of alkyltrimethylammonium halides in real samples can easily be estimated by use of this approach, which can, potentially, be extended to the semi-quantitative analysis of cationic surfactants in contaminated waste water. This approach also provides a means approximately estimating the theoretical CMCs of cationic surfactants, with errors within an order of magnitude. The reagents for preparing gold nanoparticles are, moreover, readily obtained, and preparation of the particles is extremely simple. Gold nanoparticles can be easily prepared by reducing tetrachloroaurate with sodium citrate in aqueous solution, with heating. Serial dilution with water then use of gold nanoparticles as reporter probes is a practical means of obtaining an approximate estimate of the amount of cationic surfactant in unknown samples.

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