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Investigation of the Self Assembly of Synthesized Cysteine Surfactants on Gold Nanoparticles and Their Surface Activity

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Abstract — In this work we investigate the self assembly of some synthesized alkyl cysteine surfactants on gold nanoparticles using different techniques such as UV-visible spectrum, FTIR spectra and Transmission electron microscope (TEM). The self assembly of the surfactants was effected by the alkyl chain length in the hydrophobic moiety of these surfactants. The results showed that the stabilization of gold nanoparticles was affected by the increase in alkyl chain length of these surfactants. The surface properties of the synthesized surfactants and their nanostructure with gold nanoparticles were studied using surface tension technique. The calculated surface parameters showed the effect of gold nanoparticles on the surface activity of the synthesized alkyl cysteine surfactants.

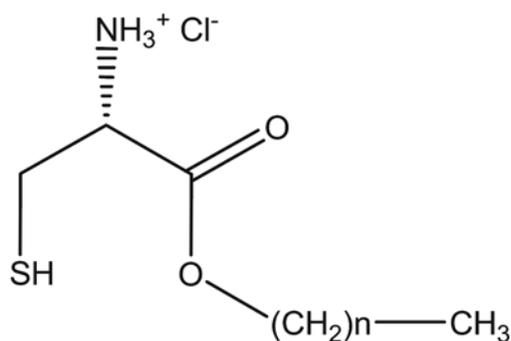
Keywords : *Alkyl cysteine surfactants, gold nanoparticles, self assembling, surface activity.*

INTRODUCTION

In the last decade, new directions of modern research, broadly defined as “nanoscale science and technology”, have emerged. These new trends involve the ability to fabricate, characterize, and manipulate artificial structures, whose features are controlled at the nanometer level. They embrace areas of research as diverse as engineering, physics, chemistry, materials science, and molecular biology. Research in this direction has been triggered by the recent availability of revolutionary instruments and approaches that allow the investigation of material properties with

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a resolution close to the atomic level [1]. Nanoscience and nanotechnology primarily deal with the synthesis, characterization, exploration, and exploitation of nanostructured materials. These materials are characterized by at least one dimension in the nanometer range. Nanostructures constitute a bridge between molecules and infinite bulk systems. Individual nanostructures include clusters, quantum dots, nanocrystals, nanowires, and nanotubes, while collections of nanostructures involve arrays, assemblies, and superlattices of the individual nanostructures [2]. Gold is the subject of one of the most ancient themes of investigation in science; its renaissance now leads to an exponentially increasing number of publications, especially in the context of emerging nanoscience and nanotechnology with nanoparticles and self-assembled monolayers (SAMs) [3]. Gold nanoparticles (AuNPs) are the most stable metal nanoparticles. AuNPs have attracted considerable attention due to their electronic, magnetic and optical properties, and their applications to catalysis and biology [4]. High affinity of organic functional groups like -SH, -CN, -COOH, -NH₂ for metallic surfaces such as Au, Cu, Ag, Pd, Pt, Hg have motivated several research groups to focus on using this phenomena for industrial applications. Self-assembled monolayers of organosulfur compounds like thiols, sulfides and disulfides on the surface of coinage metals like Cu, Ag and Au, have attracted much attention [5]. Self-assembled monolayers (SAMs) are typically formed from surfactant-like molecules which have a reactive headgroup that binds the molecules to the surface, and an organic tail of variable length and functionality. Currently most widely used and investigated model systems for self-assembly are thiols (R-SH, where R is an organic



$$n = 11, 15, 17$$

Scheme 1. The chemical structure of the synthesized alky cysteine surfactants.

residue) on gold and silanes (R-Si-OH) on SiO₂. This is partly due to the relative simplicity of the experimental procedure for making such SAMs. High quality thiol SAMs can be prepared by immersing a clean gold surface into a solution of the target compound for an extended period of up to 48 h. High quality thiol SAMs can be prepared by immersing a clean gold surface into a solution of the target compound for an extended period of up to 48 h [6]. Surface active agents (usually referred to as surfactants) are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can, therefore, be nonionic, ionic or zwitterionic, and accompanied by counter ions in the last two cases. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. The balance between hydrophobic and hydrophilic parts of the molecule gives these systems their special properties, e.g. accumulation at various interfaces and association in solution to form micelles [7].

The driving force for surfactant adsorption is the lowering of the free energy of the phase boundary. The interfacial free energy per unit area is the amount of work required to expand the interface. This interfacial free energy, referred to as surface or interfacial tension, γ , is given in m N m^{-1} . Adsorption of surfactant molecules at the interface lowers γ , and the higher the surfactant adsorption (i.e. the denser the layer) the larger the reduction in γ . The degree of surfactant adsorption at the interface depends on surfactant structure and the nature of the two phases that meet the interface [7]. True surfactants are distinguished by an ability to form oriented by monolayers at the interface (here air/water or oil/water) and, most importantly, self-assembly structures (micelles, vesicles) in bulk phases [8]. The applications of surfactants in science and industry are legion, ranging from primary processes such as the recovery and purification of raw materials in the mining and petroleum industries, to enhancing the quality of finished products such as paints, cosmetics, pharmaceuticals, and foods [9]. Cysteine is unique due to the presence of a thiol moiety in its molecule, which confers special physicochemical properties to its derivatives. Modification of cysteine residues in proteins, due to a) the participation of the thiol moiety of this amino acid in oxido-reduction reactions, b) its ability to strongly coordinate transition metal ions, or c) its nucleophilic nature and facile reaction with electrophiles, may be critically important for the design of novel types of pharmacological agents. Thus, this unique amino acid offers very interesting possibilities for developing particularly useful pharmacological agents, which generally possess a completely different mechanism of action compared with classic agents in

clinical use, thus avoiding major problems such as multi drug resistance (for antiviral and anticancer agents) or high toxicity [10]. Here in, we investigate the self assembling of some synthesized cysteine thiol surfactants namely, dodecyl cysteine hydrochloride, hexadecyl cysteine hydrochloride and octadecyl cysteine hydrochloride on gold nanoparticles. In addition, we studied the effect of gold nanoparticles on the surface activity of the synthesized surfactants.

Materials and methods :

Synthesis of the alkyl cysteine surfactants —

The compounds were synthesized by Fischer esterification between dodecyl-, cetyl-, octadecyl alcohol and cysteine hydrochloride respectively according to the previous publication [10]. An equally mole of the alkyl alcohol and cysteine hydrochloride were mixed and refluxed in 100 ml toluene for 8 hours in the presence of 1 ml HCl. The products were recrystallized twice from isopropanol and dried to give the synthesized surfactants with 98% purity. The chemical structures of the synthesized surfactants in scheme 1 were confirmed using FTIR and ^1H NMR spectra.

Synthesis of gold nanoparticles —

Gold nanoparticles (AuNPs) of ~ 25 nm size were prepared by reduction of sodium tetrachloroaurate. 2 ml of sodium tetrachloroaurate solution (1 %) was heated to boiling temperature and then 2.5 ml of tri-sodium citrate solution (1 %) was added slowly with stirring until the colour changed to winy red [11]. All solutions were prepared using pure distilled water which was obtained by passing twice-distilled water through a Milli-Q system.

Assembling of synthesized surfactants on gold nanoparticles —

The synthesized surfactants were assembled onto the surface of gold nanoparticles by mixing 20 ml of the prepared AuNPs solution with 5 ml of 1×10^{-5} M from surfactant solution and stirred at room temperature for 24 hours until the solution became colourless [5].

FT-IR spectroscopy —

All FTIR spectra were recorded with 2 cm^{-1} resolution at an angle of incidence 80° relative to the surface normal using the Fourier Transform Infrared, (ATI Mattson genesis and FTIR spectrophotometer).

UV-Visible spectrometry —

Absorption of ultra violet and visible light was performed using JENWAY 6505 UV/Vis spectrometer. The range of the wavelength of spectrum was between 400-800 nm.

Transmission Electron Microscopy —

Images of gold Nanoparticles and its nanostructures with the synthesized surfactants were carried out using TEM by placing little droplets on copper grids coated with amorphous carbon. A photographic plate of the transmission electron microscopy (Type JEOL JEM-1230 operating at 120 kV attached to a CCD camera) employed on the present work to investigate the nanostructure of the prepared samples.

Surface tension measurement —

A solution of each individual surfactant was prepared with distilled water which exhibit a surface tension of 72.1 m/Nm^{-1} . Determination of surface and interfacial tension of the solution was carried out at 25°C using Kruss Du Noüy tensiometer, Type K6 (Krüss GmbH, Hamburg, Germany) [12].

RESULTS AND DISCUSSION**Self assembly of the synthesized surfactants on gold nanoparticles**

The assembly of the synthesized surfactants was studied as follow :

FTIR spectra

The FTIR spectra of the nanostructures of the alkyl cystiene surfactants under investigation are shown in Figs. (1a-c). It was noticed that the nanostructures of the surfactants show the same peaks of the individual surfactants with slightly shift which is due to the attenuation of IR-radiation by the adsorbed AuNPs as shown in the following peaks :

NH_3^+ , 3444 cm^{-1} , C-H stretch around 3000 cm^{-1} , $\nu_{\text{as}}(\text{CH}_2)$ around 2922 cm^{-1} , $\nu_{\text{s}}(\text{CH}_2)$ around 2850 cm^{-1} , CH_2 bending around 1385 cm^{-1} , C=O ester around 1628 cm^{-1} , C-O around 1090 cm^{-1} .

UV spectrum

The UV spectrum was used to confirm the assembly of the synthesized alkyl cystiene surfactants on gold nanoparticles as shown in Fig. (2b-d). The UV spectrum of the prepared gold nanoparticles is shown in Fig. (2a). The excitation and emission spectra of the gold nanoparticles (AuNPs) is shown at $\sim 520 \text{ nm}$. This peak must arise from surface plasmon absorption of metal clusters [13]. The UV results of the nanostructure for the synthesized thiol surfactants with the AuNPs are represented in (2b-d). These results illustrate that the peak of AuNPs at $\sim 520 \text{ nm}$ is completely disappear which related to the reduction of the negative charge of the colloidal particles. Namely, metal particles in aqueous colloidal dispersions usually bear a negative charge due to adsorbed anions. The addition of neutral adsorbate molecules such as the surfactants

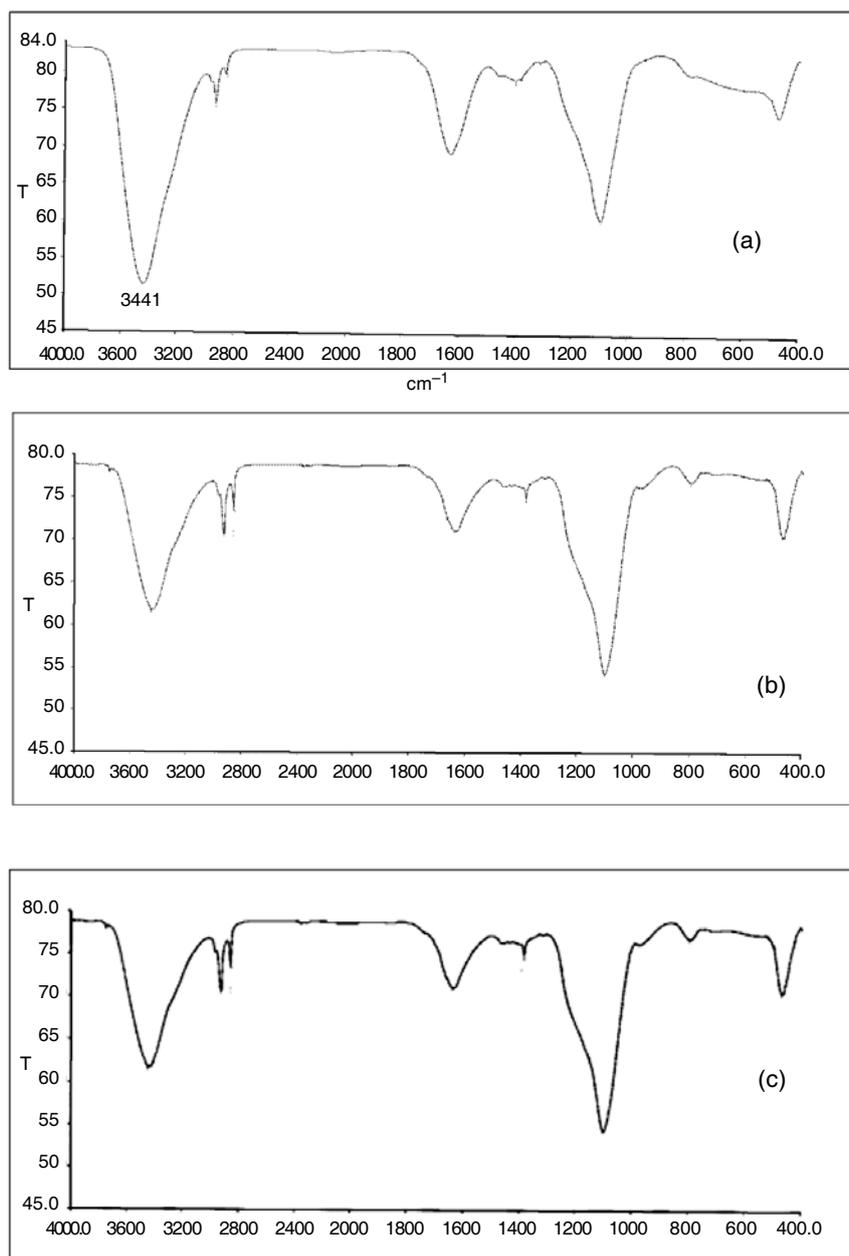


Fig. 1. FTIR of the synthesized dodecyl cysteine hydrochloride (a), hexadecyl cysteine hydrochloride (b) and octadecyl cysteine hydrochloride (c) surfactants assembled on AuNPs.

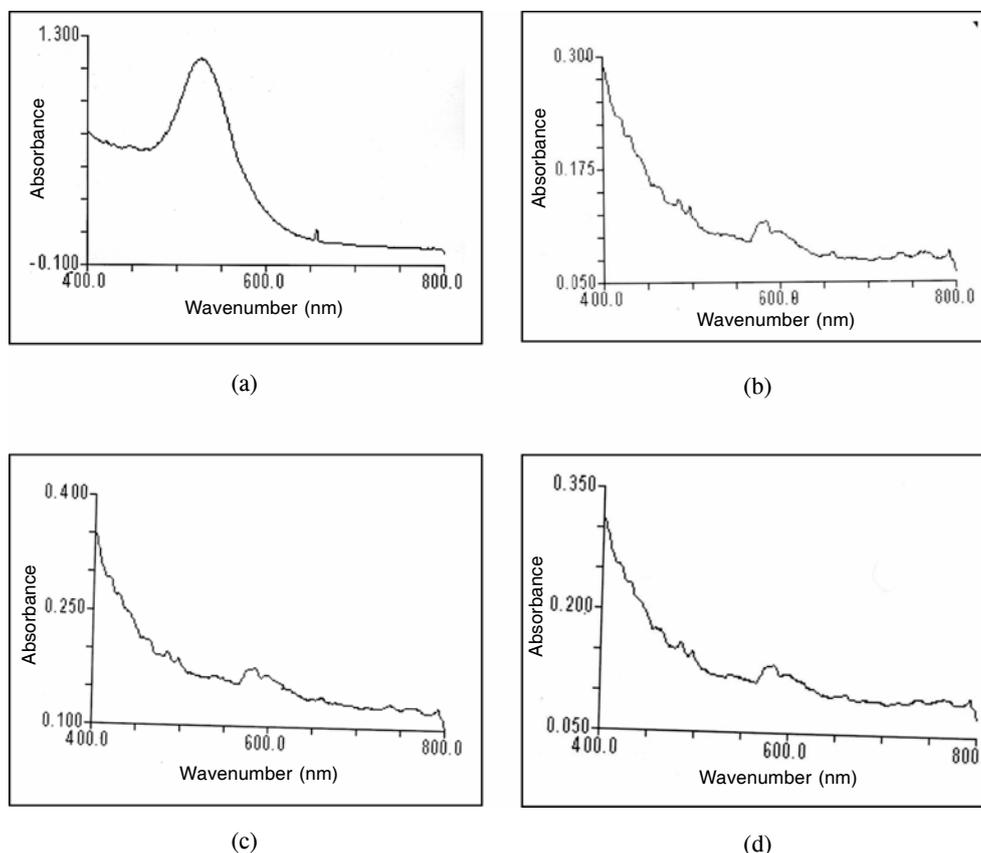


Fig. 2. UV spectroscopy of AuNPs solution (a), dodecyl cysteine hydrochloride (b), hexadecyl cysteine hydrochloride (c) and octadecyl cysteine hydrochloride (d) surfactants assembled on AuNPs.

under investigation, which displace the adsorbed ions, thus reducing the charge on the particles to the point where collisions occur as a result of diffusion motion due to the formation of nano shell of the synthesized alkyl cystiene surfactants self-assembled on the AuNPs as illustrated in our previous publication [13].

TEM

We used the TEM technique to investigate the stabilization of gold nanoparticles (AuNPs) with the synthesized alkyl cysteine surfactants and the self assembling of these surfactants on AuNPs. The TEM images of the alkyl cysteine surfactants coated AuNPs are represented in Fig. (3b-d). The TEM image in Fig. (3a) shows the small

spacing between the individual gold nanoparticles which related to their self aggregate due to the Plasmon negative charge surround the AuNPs. Comparing, the TEM in Fig. (3a-d) images it is noticed that the large spacing between the gold nanoparticles when they attached to the alkyl cysteine surfactants molecules which confirm the self assembling of the surfactant molecules on the gold nanoparticles with the formation of nanoshells. It is clear that the synthesized dodecyl cysteine hydrochloride surfactant show the best stabilization of the AuNPs as shown in Fig. (3b). This is related to

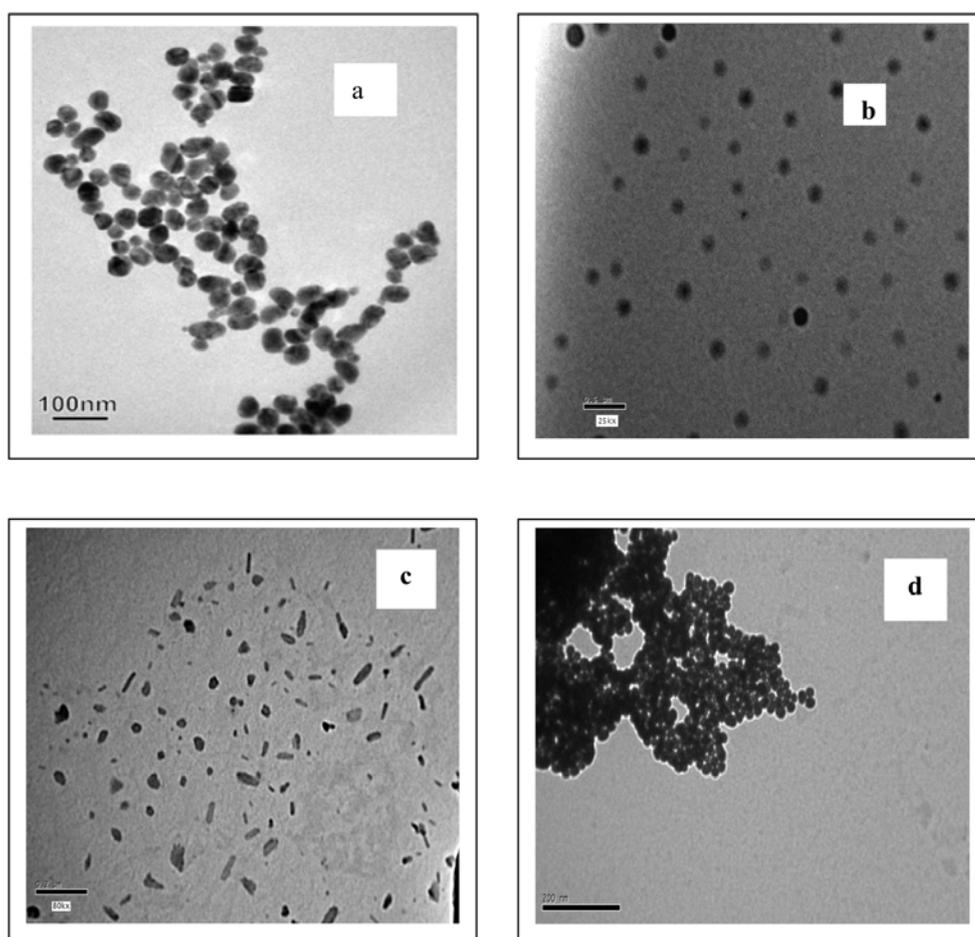


Fig. 3. TEM images of AuNPs solution (a), dodecyl cysteine hydrochloride (b), hexadecyl cysteine hydrochloride (c) and octadecyl cysteine hydrochloride (d) surfactants assembled on AuNPs.

that the adsorption of surfactant molecules to lowers the free energy of the surface and, therefore, the reactivity of the particles. The ratio of surfactant to metal precursor can control the size distribution of the nanoparticles. The steric bulk of the surfactants provide a physical barrier that prevents the metal surfaces from contacting each other directly. They can also change the surface charge of a cluster and thus change its stability toward aggregation [14]. The combination of the energetic stabilization of the metal surface by the surfactant, the consequences of charge-charge interactions, and the steric repulsion between particles prevents the system from forming aggregates. According to the above TEM results the stabilization of the gold nanoparticles size is clear after the self assembling of the surfactants molecules under investigation as shown in Fig. (3b-d).

Improvement of the surface activity of the synthesized alkyl cysteine surfactants using AuNPs

The effect of gold nanoparticles on the surface activity of the synthesized alkyl cysteine surfactants was investigated using the surface and thermodynamic parameters as shown in Table 1. The nanostructures of the synthesized alkyl cysteine surfactants with the AuNPs show more reduction in the surface tension than the individual surfactants as shown in Figs. 4a and 4b. The more reduction in surface tension by the nanostructures is related to the ability of the nanostructures of the surfactants with the AuNPs for adsorption at air/water interface and decreases the surface tension more than the individual surfactants.

The Critical micelle concentration (CMC), surface parameters (efficiency (PC_{20}), effectiveness (π_{CMC}), surface excess (Γ_{Max}), minimum area (A_{min}) and thermodynamic

TABLE 1.

Surface and thermodynamic parameters of the synthesized alkyl cysteine surfactants and their nanostructures with gold nanoparticles at 25°C.

Sample	CMC (mol/l)	γ_{cmc} (dyne/cm)	π_{CMC} (dyne/cm)	Γ_{Max} x 10 ¹⁰	A_{min} (nm)	PC_{20}	ΔG_{mic}^0 kJ/mol	ΔG_{ads}^0 kJ/mol
C12	0.00035	33.50	38.50	1.76	0.94	3.46	-19.70	-41.40
C16	0.00040	36.00	36.00	2.91	0.57	3.39	-19.40	-31.63
C18	0.00060	37.50	34.50	3.50	0.47	3.22	-18.40	-28.15
C12Au	0.00018	32.50	39.50	1.75	0.95	3.74	-21.34	-43.78
C16Au	0.00024	34.00	38.00	1.17	1.40	3.62	-20.63	-53.01
C18Au	0.00025	36.50	35.50	0.58	2.83	3.60	-20.53	-81.03

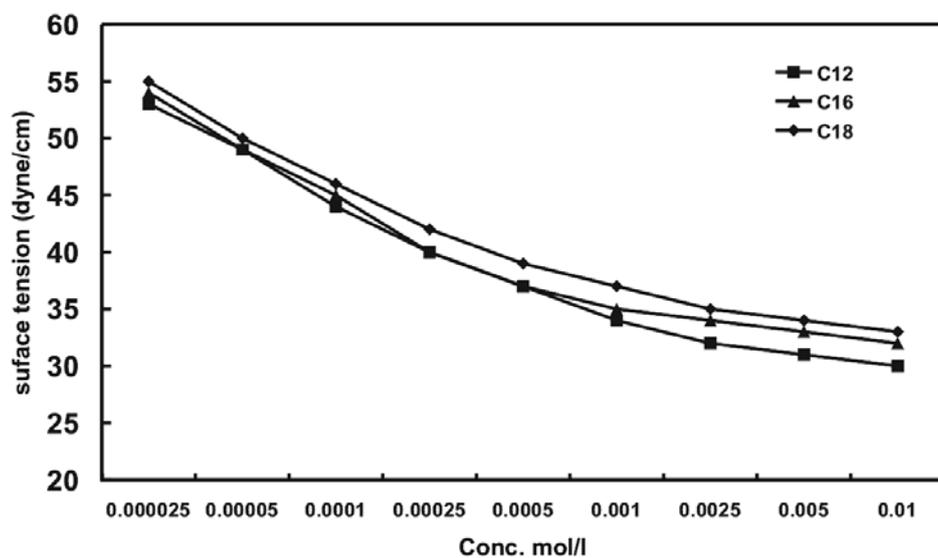


Fig. 4a. Relation between the surface tension (g) and concentration of the synthesized alkyl cysteine surfactants at 25°C.

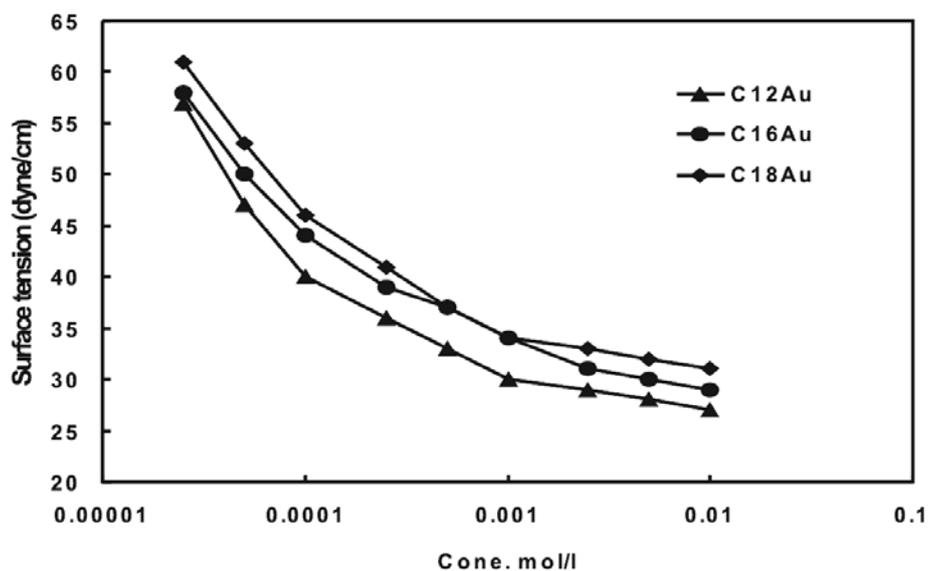


Fig. 4b. Relation between the surface tension (g) and concentration of the synthesized alkyl cysteine surfactants assembling on gold nanoparticles at 25°C.

parameters (free energy of micellization (ΔG_{mic}^0), free energy of adsorption (ΔG_{ads}^0)) of the synthesized alkyl cysteine surfactants and their nanostructures with the AuNPs listed in Table 1 were calculated according to the previous publication [12]. The results in Table 1 show improve in the CMC values of the nanostructures of the synthesized alkyl cysteine surfactants than the individual surfactants. The decrease in CMC values indicates the enhancement in the solubility of the surfactants under investigation when assembling on gold nanoparticles.

The effectiveness (π_{CMC}) results in Table 1 reveal that the nanostructures of the synthesized alkyl cysteine surfactants with AuNPs have high effectiveness values than the individual surfactants which indicating the ability of these nanostructures toward adsorption at air/water interface and decrease the surface tension more than the individual surfactants under investigation. The effectiveness results are compatible with the efficiency (PC_{20}) values in Table 1 which illustrate the improvement in the surface activity of the surfactants under investigation after assembled on gold nanoparticles. The study of surface excess (Γ_{max}), minimum area (A_{min}) data in Table 1 show that the as the surface excess decrease the minimum area increase which related to the ability of the surfactant molecules towards the adsorption at air/water interface. The minimum area of the nanostructures of the synthesized alkyl cysteine surfactants increase than that of the individual surfactants which may be due to the different in the orientation of the surfactant molecules when assembled on gold nanoparticles that effect on the adsorption of these molecules at air/water interface.

Further investigation of the effect of the gold nanoparticles on the surface activity of the synthesized alkyl cysteine surfactants can be illustrated from the thermodynamic results in Table 1. The micellization process of these surfactants and their nanostructure with AuNPs is spontaneous because the free energies of micellization (ΔG_{mic}^0) are all negative values. In general the ΔG_{mic}^0 values of the nanostructures of the surfactants with AuNPs are increased than that of the individual surfactants. This means that, the nanostructure of the synthesized surfactants activate the micellization process and increase the solubility of these surfactants in aqueous solution. Also, it is noticed that the ΔG_{ads}^0 values of the nanostructures of these surfactants are more negative than that of the individual surfactants, which indicate that the nanostructures of the alkyl cysteine surfactants with AuNPs are favor adsorption at air/water interface more than the individual surfactants. According to the all above results from Table 1 it can be conclude that the assembling of the synthesized alkyl cysteine surfactants on gold nanoparticles has improve their surface activity.

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