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# Synthesis and Biological Activity of (Tetrahalo Metallate) Copper and Nickel Nanoparticles Stabilized by Cationic Thiol Polyurethane Surfactants

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**Abstract:** Copper and nickel nanoparticles are known to be one of the multifunctional inorganic nanoparticles with effective antibacterial activity. This study aims to determine the antimicrobial efficacy of chemical synthesized copper and nickel nanoparticle against various bacterial and fungal pathogens. Grinding method is used to synthesize copper and nickel nanoparticles. In this paper, the new cationic thiol polyurethane surfactants with different alkyl chain length were synthesized (PQ8, PQ10 and PQ12). The chemical structure of the synthesized surfactants was confirmed using infra-red spectroscopy (IR) and proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR). The nanostructure of the synthesized surfactant with copper and nickel nanoparticles with diameters ranging from 10 to 55 nm was prepared and characterized using ultra violet spectrophotometer (UV), infra-red spectroscopy (IR) and transmission electron microscope (TEM). The results declare formation and stabilization of copper and nickel nanoparticle using synthesized cationic surfactants. Antimicrobial activity of the synthesized cationic surfactants and their nanostructure with copper and nickel nanoparticles were evaluated against pathogenic bacteria and fungi. The antimicrobial activity showed the enhancement in the antimicrobial activity of the synthesized cationic surfactants in the nanostructures form.

**Keywords:** Polyurethane, Cationic surfactants, Copper nanoparticles, Nickel nanoparticles, Antimicrobial activity, Transmission electron microscope.

## 1. Introduction

Cationic polyurethane dispersions, which are prepared by incorporating a tertiary amine diol or polyol followed by treatment with an acid, are seldom used commercially. One potential advantage of cationic polyurethane dispersions is that they have been found to exhibit excellent adhesion properties. However, the antibacterial properties of cationic polyurethane dispersions are of much greater interest. Cationic compounds are able to bind to bacteria and other microbes and disrupt cell structure, resulting in permeabilization and death [1].

Polymeric materials containing quaternary ammonium have been extensively studied and used in antibacterial-relevant application [2]. It's found that the positively charged quaternary ammonium groups destructively interact with negatively charged bacterial cells and/or cytoplasmic membranes. The rise of quaternary ammonium groups improves the antibacterial activity of the polyurethane dispersions [3].

In recent years, the synthesis and utilization of novel antimicrobial cationic surfactants and their nanoparticles has increased due to the gradual increase of drug resistance among microorganisms. For this reason, copper and nickel compounds have also been employed as antimicrobial and antifungus agents. By using nanotechnology, which enhances the antimicrobial activity of copper and nickel metal by manipulating it to the nanoparticles, copper and nickel nanoparticles have been widely used to control bacterial and fungal diseases. [4-5].

Copper, nickel and the compounds of Au, Ag, Pd and Pt are widely used in these days. Copper and nickel have an excellent electrical conductivity. Due to relatively low costs, this metal plays a significant role in modern electronic circuit [6]. Because of its excellent electrical conductivity, catalytic behaviour, good compatibility and surface enhanced Raman scattering activity. Copper and nickel nanoparticles have drawn the attention of scientists to be used as essential component in the future nano-devices [7]. Cu and Ni nanowires are used in nano electronics and have application possibilities for magnetic devices, nano sensors, electron emitters and other electronic applications. Cu and Ni nanoparticles have been explored to be used as nano probes in medicines and bio-analytical areas [8-9].

The emergence of nanoscience and nanotechnology in the last decade presents opportunities for exploring the bactericidal effect of metal nanoparticles. The bactericidal effect of metal nanoparticles has been attributed to small size and high surface to volume ratio, which allows them to interact closely with microbial membranes and not merely due to the release of metal ions in solution [10].

In the present study stable copper and nickel nanoparticles with narrow size and homogenous distribution were synthesized by grinding method and cationic thiol polyurethane surfactants used as a capping agent. Even today, the exact mechanism of antimicrobial action of the CuNPs remains unknown. The general view seems to be a combination of several factors: releasing  $\text{Cu}^{+2}$  ions, their penetration and disruption cell membrane and biochemical pathway by chelating cellular enzymes and DNA damage [11-

12].

Previously reported antibacterial activity of copper nano particle, it was found that it has significant potency to act as bacteriocidal agent than gold, silver, zinc nano particles. Combination of different nano particles such as silver and copper may show more significant effect on bacterial growth. Gram-positive bacteria have a thick cell wall containing multiple layers of peptidoglycan, while gram-negative bacteria have a relatively thin cell wall consisting of a single layer of peptidoglycan. Surfaces of copper nano particles interact directly with the bacterial cell wall and outer membrane, leads to rupture of cell wall and killing bacteria [13-14].

## 2. Materials and Methods

### 2.1. Materials

Fatty alcohols (Octanol, Decanol and Dodecanol) were purchased from Sigma, Germany. Toluene diisocyanate TDI (97 %) was purchased from DOW, USA. Mercapto acetic acid, Bromoacetic acid and Sodium borohydride were purchased from Aldrich, Germany. Copper Chloride and Nickle chloride were purchased from BDH, British. Triethanol amine and solvents were obtained from ADWIC chemicals company, Egypt.

### 2.2. Instrumentation

Elemental analysis: Varian Elementary Analyzer; FTIR spectroscopy: Perkin Elmer Genesis Fourier Transformer FTIR measured at 4000-400 ( $\text{cm}^{-1}$ ) applying potassium bromide compressed thin pellet technique. The nuclear magnetic resonance spectra were measured by Varian NMR-300, Mercury 300 MHz spectrometers using  $\text{CDCl}_3$  as solvent and trimethyl silane (TMS) as a reference to determine the different chemical shifts  $\delta(\text{ppm})$ ; GPC measurements were performed using GPC-7890A instrument equipped with DB-23 column, 60 mm x 0.25 mm, i.d. of 0.25  $\mu\text{m}$ . TEM images were performed using TEM-JEOL JEM-2000, Germany.

### 2.3. Synthesis

#### 2.3.1. Preparation of triethanol amine mono mercaptoacetate

Triethanol amine (0.1 mole) and mercaptoacetic acid (0.1 mole) were charged in 250 mL round flask in presence of xylene (75 mL) as a solvent and *p*-toluene sulfonic acid (0.1 g) as a dehydrating agent. The completion of the reaction was monitored by obtaining 0.1 mole of  $\text{H}_2\text{O}$  (1.8 mL) [15]. At the end of the reaction, the solvent was removed by evaporated by the effect of evacuation, while *p*-toluene sulfonic acid was eliminated from the reaction medium by take out the obtained esters by dissolving in ether (diethyl ether). The evaporated solvent was recovered and purified to reuse. The unreacted and excess reactants were eliminated from the products by successive sanitization of the crude products to afford triethanol

amine mono mercaptoacetate in a yield of 96%.

### 2.3.2. Preparation of thiol polyurethane (P)

Thiol polyurethane polymerization reaction was carried out in a suitable flat bottom glass reactor (500 mL) connected to a mechanical rotor, dropping funnel, thermometer and condenser. Inside the reaction vessel, a mixture of toluene diisocyanate (TDI) (0.1 mole) dissolved in methyl ethyl ketone (50 mL), triethanol amine mercaptoacetate (0.2 mole) and five drops of triethylene diamine dropped during 20 min was mixed [16]. The reaction medium was continuously mixed at 30 °C for 30 min to obtain the pre-polymer. The ratio of isocyanates (NCO) to reactive hydroxyl group (OH) was reserved at 1:2 in polyurethane reaction polymerization. The prepared polymer was washed twice using appropriate amounts of methyl ethyl ketone and finally dried (yield 92%).

### 2.3.3. Preparation of fatty esters bromoacetate (Q8, Q10 and Q12)

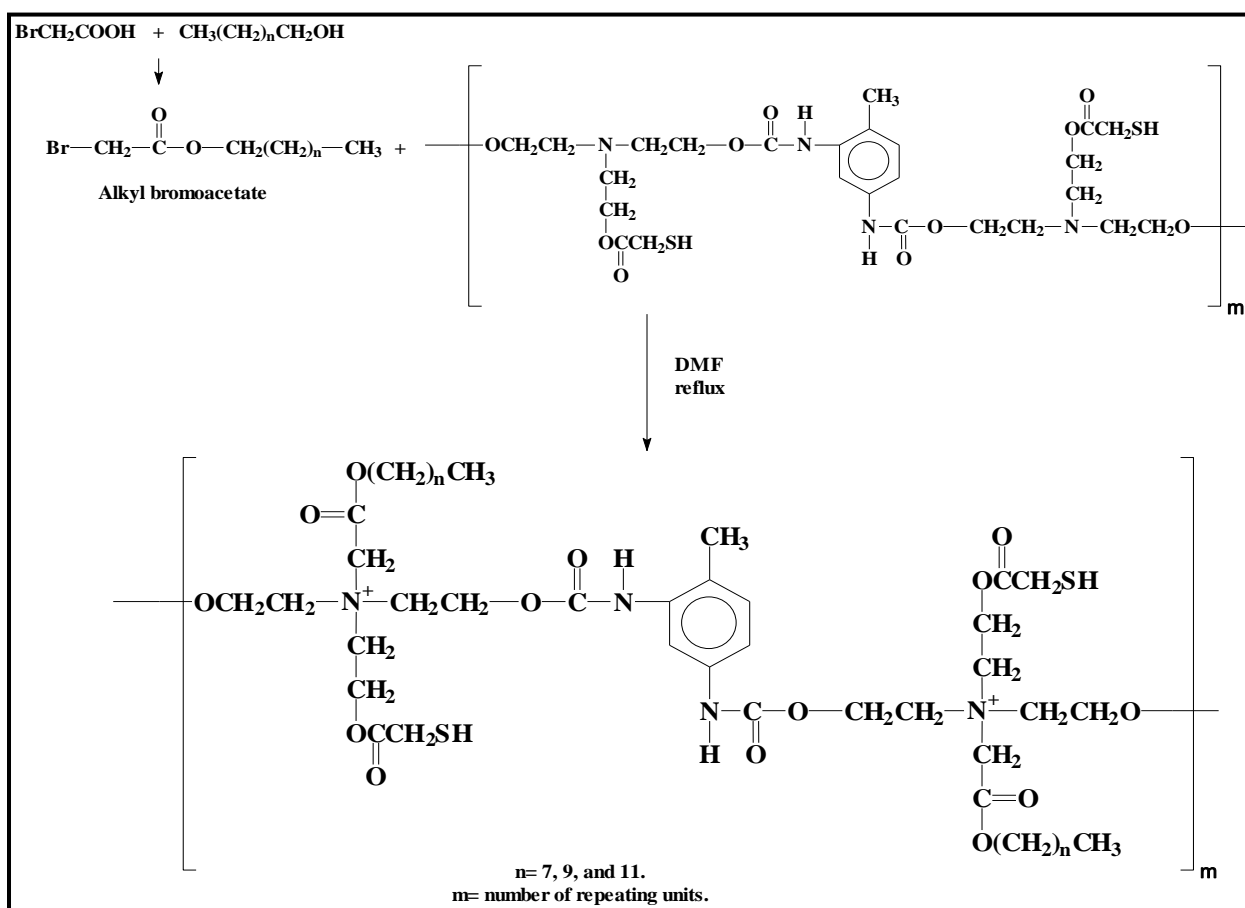
Fatty esters bromoacetate (Q8, Q10 and Q12) were prepared throughout reacting different fatty alcohols (0.1 mole) namely: octanol, decanol and dodecanol and bromoacetic acid (0.1 mole) in the presence of xylene (100 mL) as a solvent and *p*-toluene sulphonic acid (0.01 wt%) as dehydrating agent under heating and stirring conditions until the expected amount of water (1.8 mL) is produced. At the end of the reaction, xylene was stripped off using reduced pressure; *p*-toluene sulphonic acid was eliminated by extracting the product from diethyl ether and the solvent was removed [17] to afford the different fatty esters bromoacetate (yield 95-98%).

### 2.3.4. Preparation of cationic thiol polyurethane surfactants (PQ8, PQ10 and PQ12)

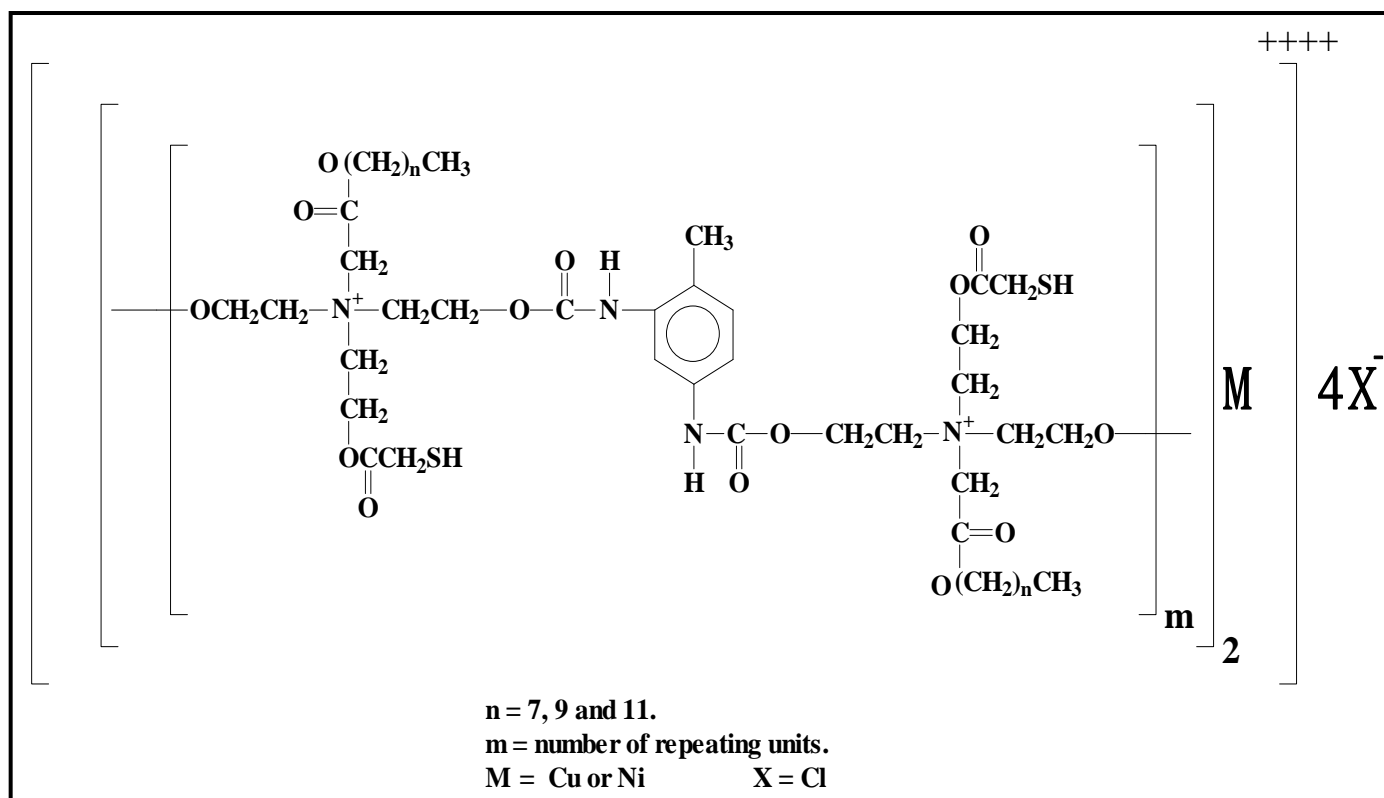
Cationic thiol polyurethane surfactants were prepared by refluxing equimolar amounts of thiol polyurethane (P) and octyl, decyl, dodecyl esters (Q8, Q10 and Q12) individually in a suitable amount of dimethyl formamide (DMF) for 20 h. The produced compounds were filtered off, washed by excess DMF, and dried under reduced pressure at 50 °C to afford yellow to brown viscous liquids designated as: PQ8, PQ10 and PQ12 (yield 82-89%) [18-19] (**Scheme 1**).

### 2.3.5. Synthesis of nano cationic thiol polyurethane tetrahalo metallate PQ-M NPs

By grinding (0.1 mole) of copper chloride dihydrate and nickel chloride hexahydrate with (0.2 mole) of cationic thiol polyurethane surfactants in the mortar until all components mixed well. After then ethanoic solution of the previous mixture was refluxed under magnetic stirring for about 2 hours to produce tetra halo metallate complexes and this indicate by change the color of mixture. The product was poured into a flat plate and dried in the hood, washed with alcohol twice and dried. The product is believed to have the structure in (**Scheme 2**) [20-21].



Scheme 1: Synthesis of cationic thiol polyurethane surfactants (PQ)



Scheme 2: Nano cationic thiol polyurethane tetrahalo metallate PQ-M NPs

### 3. Biological Activity

The antimicrobial activity of synthesized cationic thiol polyurethane surfactants and their nanostructures with copper and nickel nanoparticles were measured against a wide range of test-organisms comprising: bacteria and fungi.

#### 3.1. The Media

The following media used in the antimicrobial activity of synthesized products, the bacterial species grow on nutrient agar, while fungi mold grow on Czapek's dox agar. (a) Nutrient agar: Nutrient agar consists of Beef extract (3.0 g/l); peptone (5.0 g/l), sodium chloride (3.0 g/l) and agar (20.0 g/l), then, completes the volume to 1 l, heated the mixture until the boiling and sterilizes the media by autoclave. (b) Czapek's Dox agar: Czapek's Dox agar consists of sucrose (20.0 g/l), sodium nitrate (2.0 g/l), magnesium sulfate (0.5 g/l), potassium chloride (0.5 g/l), ferrous sulfate (0.01 g/l) and agar (20.0 g/l), then, complete the volume to 1 l, the mixture was heated to boiling, and then the media was sterilized by autoclave.

#### 3.2. Microorganisms

The different species of tested organisms were obtained from the unit of Operation Development Center, Egyptian Petroleum Research Institute. The used microorganisms were Gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*), Gram-negative bacteria (*Salmonella typhimurium* and *Escherichia coli*), Yeast and Fungi (*Candida albicans* and *Aspergillus niger*). An assay is made to determine the ability of an antibiotic to kill or inhibit the growth of living microorganisms, the technique which used is: filter-paper disk-agar diffusion (Kirby-Bauer) are as the following [22]:

- (1). Inoculate flask of melted agar medium with the organism to be tested.
- (2). Pour this inoculated medium into a Petri dish.
- (3). After the agar has solidified, a multilobed disk that impregnated with different antibiotics laid on top of agar.
- (4). The antibiotic in each lobe of disk diffuses into medium and if the organism is sensitive to a particular antibiotic, no growth occur in a large zone surrounding that lobe (clear zone).
- (5). The diameters of inhibition zones were measured after 24–48 h at 35–37 C (for bacteria) and 3–4 days at 25–27 C (for yeast and fungi) of incubation at 28 C
- (6). Measure each clear zone and compare between them to determine the antibiotic which is more inhibitor.

Chloramphenicol, cycloheximide and cephalothin were used as reference drugs for gram-positive bacteria, gram-negative bacteria, and fungi, respectively.

Chloramphenicol is abroad spectrum antibiotic which acts as a potent inhibitor of bacterial protein biosynthesis. It has along clinical history but bacterial resistance is common. Chloramphenicol foot printing

studies with specific nucleotides has revealed the binding sites to be on the 50S ribosomal subunit where chloramphenicol interacts with the central loop of 23S rRNA domain V to inhibit peptidyl transferase activity [23].

Cycloheximide is a glutarimide antibiotic that inhibits protein biosynthesis in systems that utilize ribosomes of the 80 S type. The inhibition has been shown to involve one or more steps in the reaction sequence by which amino acids are transferred from aminoacyl transfer RNA into nascent peptides on ribosomes [24].

Cephalothin is bactericidal, effective against Gram-positive and Gram-negative bacterial species in vitro and in vivo, devoid of inherent toxicities and resistant to degradation by staphylococcal penicillinase. Cephalothin is chemically related to the penicillins, but does not produce crossed allergic hypersensitivity reactions [25].

## 4. Results and Discussion

### 4.1. Chemical Structure

**Scheme 1** represents the preparation of cationic thiol polyurethane surfactants.

**Scheme 2** represents the preparation of nano cationic thiol polyurethane tetrahalo metallate.

The elemental analysis of the prepared cationic polyurethane surfactants (**Table 1**) showed the comparable values of the predicted and obtained ratios of the different elements in their chemical structure. The chemical structures of the prepared cationic polyurethane surfactants were confirmed using molecular weight measurements, elemental analysis, FTIR spectroscopy and <sup>1</sup>HNMR spectroscopy.

**Table 1:** Elemental analysis of the synthesized cationic thiol polyurethane surfactants

| Compound    | M.wt*<br>g/mole | Formula   | C%    |       | H%    |       | N%    |       | S%    |       | Br%   |       |
|-------------|-----------------|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|             |                 |   | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| <b>PQ8</b>  | 20500           | (C <sub>45</sub> H <sub>78</sub> O <sub>14</sub> N <sub>4</sub> S <sub>2</sub> Br <sub>2</sub> ) <sub>n</sub> | 46.47 | 46.42 | 6.65  | 6.66  | 5.56  | 5.53  | 6.35  | 6.30  | 15.89 | 15.85 |
| <b>PQ10</b> | 21400           | (C <sub>49</sub> H <sub>86</sub> O <sub>14</sub> N <sub>4</sub> S <sub>2</sub> Br <sub>2</sub> ) <sub>n</sub> | 48.54 | 48.50 | 7.05  | 7.06  | 5.27  | 5.25  | 6.02  | 5.98  | 15.05 | 15.01 |
| <b>PQ12</b> | 22300           | (C <sub>53</sub> H <sub>94</sub> O <sub>14</sub> N <sub>4</sub> S <sub>2</sub> Br <sub>2</sub> ) <sub>n</sub> | 50.36 | 50.31 | 7.41  | 7.43  | 5.00  | 4.97  | 5.71  | 5.68  | 14.28 | 14.25 |

\* Obtained molecular weight from GPC measurements, n≈18.

#### 4.1.1. FTIR Spectroscopic analysis

The chemical structures of the prepared cationic surfactants and their intermediates were confirmed using FTIR spectroscopic analysis.

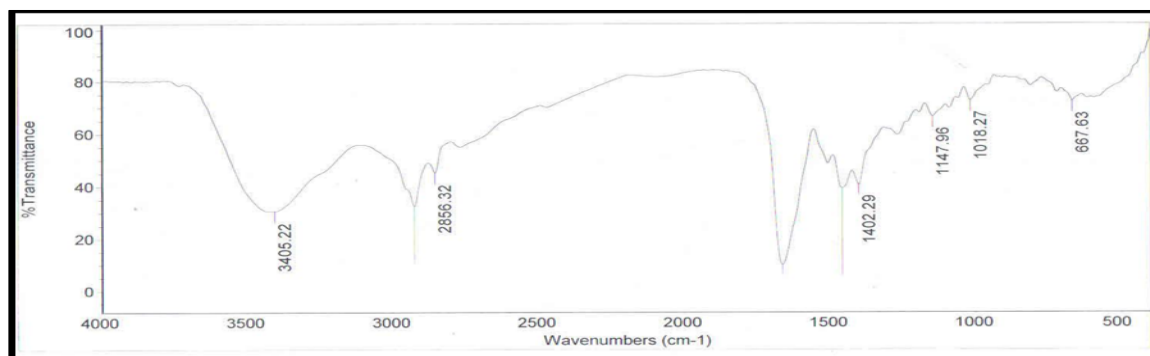
FTIR spectra of triethanol amine mercaptoacetate showed the following absorption bands: broad absorption band centered at 3435 cm<sup>-1</sup> corresponds to -OH stretching; weak absorption band at 2550 cm<sup>-1</sup>

corresponds to stretching of S-H group; absorption band at  $2932\text{ cm}^{-1}$  attributed to symmetric stretching of C-H group;  $1018\text{ cm}^{-1}$  corresponds to C-N stretching group of aliphatic amine and absorption band at  $1732\text{ cm}^{-1}$  corresponds to C=O ester group.

Thiol polyurethane compound (**P**) showed the following absorption bands:  $1663\text{ cm}^{-1}$  corresponds to C=O of urethane group;  $1510\text{ cm}^{-1}$  corresponds to N-H binding of urethane group;  $1461\text{ cm}^{-1}$  described for the double bonds in the phenyl moiety (C=C) in toluene diisocyanate moiety (TDI).

FTIR spectra of alkyl bromoacetate esters (**Q8, Q10 and Q12**) represented the disappearance of the broad band at  $3400\text{ cm}^{-1}$  of alcoholic hydroxyl groups of the reacted fatty alcohols, the appearance of new absorption bands at:  $1736\text{-}1738\text{ cm}^{-1}$  corresponds to carbonyl ester indicates the ester (Q8, Q10 and Q12) formation;  $1275\text{-}1277\text{ cm}^{-1}$  corresponds to ether linkages C-O-C;  $2920\text{-}2922\text{ cm}^{-1}$  and  $2849\text{-}2850\text{ cm}^{-1}$  corresponded to symmetric and asymmetric stretching of C-H groups. The characteristic absorption band of C-Br bond was appeared in the range of  $663\text{-}667\text{ cm}^{-1}$ .

FTIR spectra of the prepared cationic thiol polyurethane surfactants (**PQ8, PQ10 and PQ12**) showed similar absorption bands to the absorption bands of triethanol amine mercaptoacetate, thiol polyurethane and alkyl bromoacetate esters. Furthermore, IR spectra recorded a disappearance of the absorption band at  $660\text{ cm}^{-1}$  and the appearance of a new absorption band at  $1460\text{ cm}^{-1}$  and  $2960\text{ cm}^{-1}$  corresponding to vibration and elongation of  $[\text{C-N}^+]$  group (**Figure 1**).

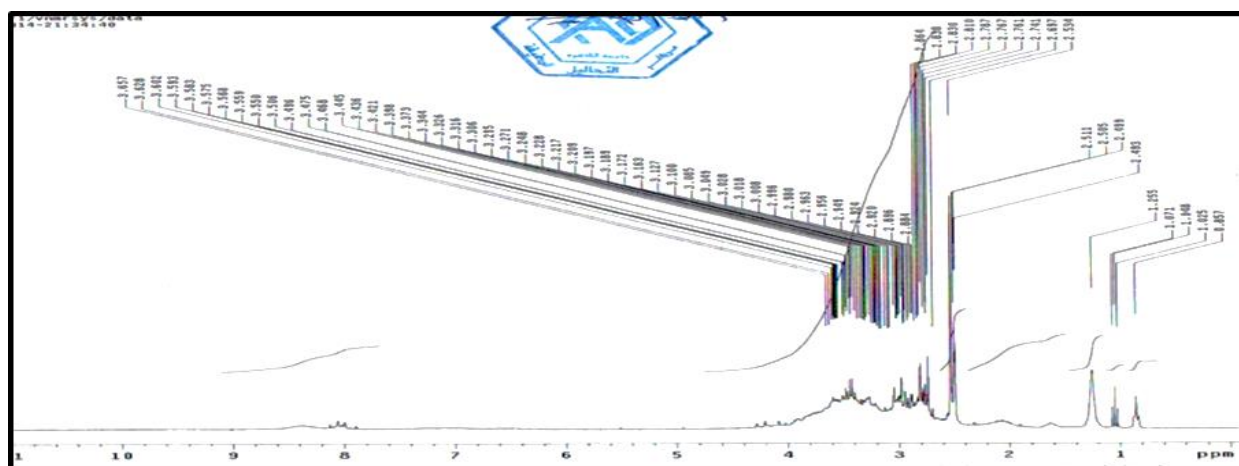


**Figure 1:** IR spectra of cationic thiol polyurethane surfactant PQ10

#### 4.1.2. $^1\text{H-NMR}$ Spectroscopic analysis

The  $^1\text{H}$  NMR spectra of the synthesized cationic surfactants (**Figure 2**) for PQ10 as representative for the prepared surfactants) showed the appearance of signals at:  $\delta = 0.85\text{ ppm}$  (t, 3H,  $\text{CH}_3$ ) assigned to terminal methyl group;  $1.25\text{ ppm}$  (m, nH,  $\text{CH}_2$ ) attributed to the methylene groups of the fatty chains;  $2.5\text{ ppm}$  (t, 3H,  $\text{CH}_3\text{Ph}$ ) assigned to methyl group of toluene diisocyanate moiety;  $7.8\text{ ppm}$ ,  $8.0\text{ ppm}$  and  $8.2\text{ ppm}$  (m, 4H, phenyl group).





**Figure 2:**  $^1\text{H}$ -NMR spectra of cationic thiol polyurethane surfactant PQ10

#### 4.1.3. Molecular weight measurements

The molecular weights of the prepared cationic surfactants were determined using GPC chromatographic measurements according to the methodology of our colleague [26]. The results showed that the surfactant molecules contain an average of 18 repeated units (exactly 17.8 units). The obtained values of the molecular weights of the different surfactants were listed in **Table 1**.

#### 4.1.4. UV-Vis Spectroscopy

UV-Vis absorption spectra were used to determine the formation of copper and nickel nanoparticles stabilized by different cationic thiol polyurethane surfactants. UV-Vis absorption spectra of the prepared copper and nickel nanoparticles stabilized by different cationic thiol polyurethane surfactants were recorded in water as a solvent in order to monitor their formation and stability. Cationic thiol polyurethane surfactants with copper and nickel nanoparticles were confirmed by the appearance of new bands in UV spectra. UV-Vis spectroscopy is quite sensitive to the formation of copper and nickel nanoparticles due to surface Plasmon excitation.

UV spectrum of copper nanoparticles for characterizing the metallic nature whose broad peak corresponds to the Cu range from 350–550 nm [10].

UV spectrum of nickel nanoparticles for characterizing the metallic nature whose broad peak corresponds to the Ni range from 250–370 nm [27].

**UV-Vis spectra** shows absorption spectra of Cu NPs and Ni NPs capped by prepared cationic surfactants, which show absorption band listed in **table 2** which an indication on formation copper and nickel nanoparticles, due to surface Plasmon resonance of copper and nickel nanoparticles.

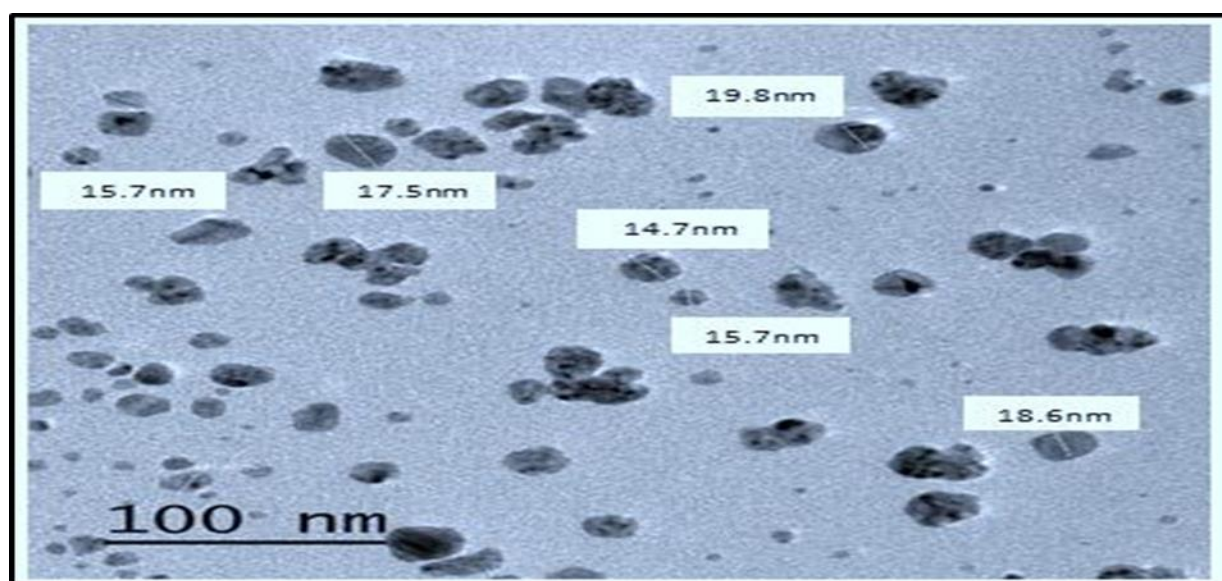
**Table 2:** UV absorption maxima of copper and nickel nanoparticles with cationic thiol polyurethane surfactants

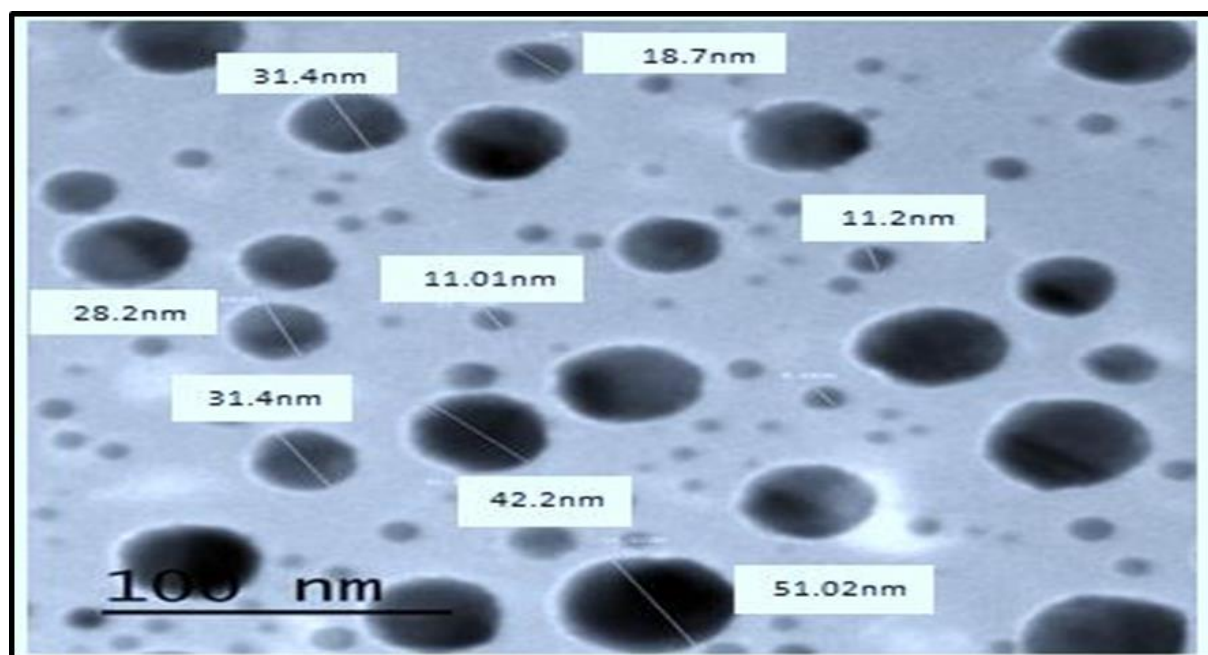
| Compounds    | $\lambda_{\max}$ (nm) |
|--------------|-----------------------|
| PQ8-Cu NPs   | 314, 389              |
| PQ10- Cu NPs | 310, 400              |
| PQ12- Cu NPs | 310, 402              |
| PQ8-Ni NPs   | 224, 296              |
| PQ10- Ni NPs | 220, 316              |
| PQ12- Ni NPs | 210, 308              |

Bands at  $\lambda_{\max}$  range from 210 to 314 nm characteristic for the used capping agents, which matches with the band, appeared for aqueous solution of the used capping agents alone. It is known that the amount and size of copper and nickel nanoparticles are positively related with the adsorption peak intensity and the  $\lambda_{\max}$  on the UV–Vis spectra respectively.

#### 4.1.5. TEM Spectroscopy

TEM spectroscopy determines the size and morphology of the formed nanoparticles. The size and morphology of the prepared copper and nickel nanoparticles stabilized by cationic thiol polyurethane surfactants were investigated using transmission electron microscope (TEM), **Figures 3a and 3b** (as representative for the prepared copper and nickel nanoparticles). It is clear from TEM images that the copper and nickel nanoparticles stabilized by cationic thiol polyurethane surfactants are predominantly spherical in shape and polydispersed. The TEM image showed the self-assembling of the prepared surfactant on the copper and nickel nanoparticles which causes the stabilization of the nano size of these nanoparticles due to the formation of nano shells with the used surfactant.

**Figure 3a:** TEM images of Cu NPs with PQ12



**Figure 3b:** TEM images of Ni NPs with PQ12

#### 4.2. Antimicrobial and antifungal activity of the synthesized cationic surfactants and their nanostructures

The biological activities of the synthesized cationic surfactants (PQ8, PQ10 and PQ12) and their nanostructures with copper and nickel nanoparticles was screened against pathogenic Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*), Gram-negative (*Salmonella Typhimurium* and *Escherichia coli*), bacteria and also, some pathogenic fungi (*C. albicans* and *Aspergillus niger*) using the values of the inhibition zone diameter tests and the results are summarized in **Table 3**. Data in **Table 3** indicating that the synthesized compounds have antimicrobial activity rang from a moderate to slight high effect on Gram negative bacteria and Gram positive bacteria and moderate effect on fungi and high effect on yeast compared to the drug reference used.

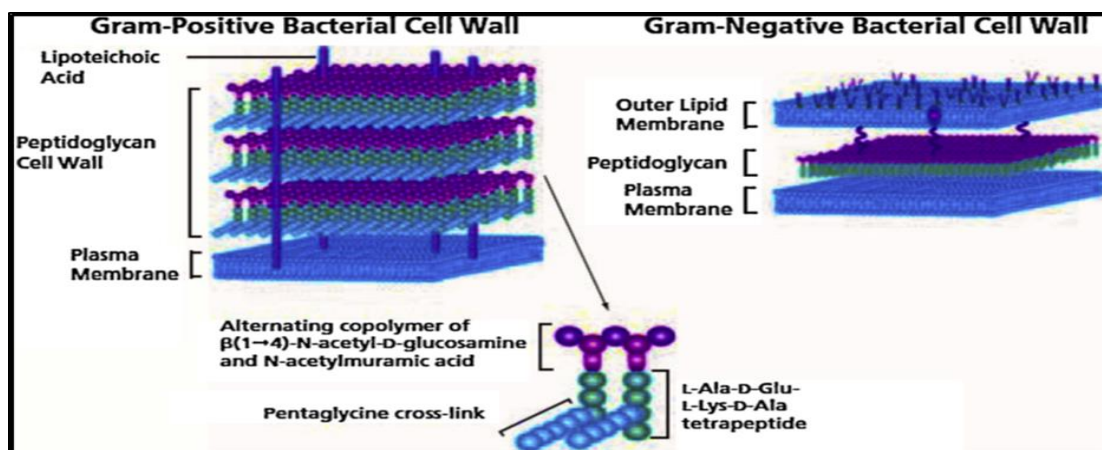
**Table 3:** Antimicrobial activity of synthesized surfactants against pathogenic bacteria, yeast and fungi

| Compounds      | Bacteria          |                       |                        |                  | Yeast            | Fungi             |
|----------------|-------------------|-----------------------|------------------------|------------------|------------------|-------------------|
|                | Gram positive     |                       | Gram negative          |                  | Candida albicans | Aspergillus niger |
|                | Bacillus subtilis | Staphylococcus aureus | Salmonella typhimurium | Escherichia coli |                  |                   |
| <b>Control</b> | 26                | 25                    | 28                     | 27               | 28               | 26                |
| PQ8            | 15                | 0                     | 0                      | 10               | 17               | 0                 |
| PQ10           | 17                | 9                     | 0                      | 14               | 19               | 0                 |
| PQ12           | 22                | 14                    | 0                      | 16               | 24               | 0                 |
| PQ8-Cu NPs     | 20                | 20                    | 17                     | 18               | 15               | 0                 |
| PQ10-Cu NPs    | 29                | 21                    | 21                     | 26               | 18               | 16                |
| PQ12-Cu NPs    | 35                | 41                    | 33                     | 32               | 23               | 16                |
| PQ8-Ni NPs     | 23                | 26                    | 22                     | 21               | 23               | 16                |
| PQ10-Ni NPs    | 27                | 29                    | 27                     | 25               | 24               | 14                |
| PQ12-Ni NPs    | 32                | 25                    | 34                     | 20               | 25               | 18                |

It is clear that the antimicrobial activities are gradually increased by increasing the hydrophobic chain length. The PQ12 surfactant showed the maximum antimicrobial activities against the tested bacterial strains. That behavior is depending on the surface activities of these biocides. Increasing the hydrophobic chain length increases the adsorption tendency of the biocide molecules at the various surfaces (water or microorganism's membranes). Hence, the potent action of the molecules is increased due to their high population at the cellular membrane [28-29].

General observation for data in **Table 3** indicates that the Gram- positive bacteria are more resistant to the tested compounds compared with the Gram-negative bacteria. The data provided from the inhibition zone diameter are describing the general behavior of the tested biocides against the different bacterial genera. The results of the antifungal activity obtained from the biological study showed promising features of the tested biocides against the most pathogenic fungal strain (*C. albicans*).

The bacterial cell membrane is composed of a thick wall containing many layers of peptidoglycan and teichoic acids, which are glycerol-ribitol (polyhydric alcohol) through a phosphorus bond surrounded by lipids of lipopolysaccharides and proteins [30]. In Gram positive bacteria (**Figure 4**), the adsorption is occurred in the lipoteichonic acid layer which is characterized by the charged nature and the ability to interact with the positively charged molecules. While in the Gram-negative bacteria (**Figure 4**), the lipid layer (highly nonpolar layer) is the target of the positively charged biocide molecules. So the mode of action of that type of compounds on different microorganisms can be attributed to the adsorption of amphiphile molecules on the outer cellular membrane of the microorganism due to their amphipathic characteristics. In addition the similarity between the hydrophobic chains and the lipid layers and the building units of the cell membranes and the monosaccharide in these compounds [31]. As a result of that adsorption, the molecules penetrate through the cell membrane; furthermore the positive charges in the cationic molecules neutralize the negative charges on the bacterial cell membranes. Accordingly, the selective permeability which characterizes the outer cellular membrane is completely deactivated [32].



**Figure 4:** Structure of the bacterial cell walls

Hence, the vital transportation of essential components, bioreactions and activities of the cell are disturbed, causing death for these microorganisms.

By inspection data in **Table 3**, the biological activity of copper and nickel nanoparticle stabilized by synthesized cationic surfactants higher than corresponding synthesized cationic surfactants, this can be attributed to copper and nickel nanoparticle alone have biological activity, so prepared surfactant capped copper and nickel nanoparticles have higher activity, this can be attributed to the higher surface area of prepared nanoparticles. In addition to the bactericidal effect of metal nanoparticles has been attributed to their small size and high surface to volume ratio, which allows them to interact closely with microbial membranes and is not merely due to the release of metal ions in solution. A cell wall is present around the outside of the bacterial cell membrane and it is essential to the survival of bacteria.

## 5. Conclusion

The main conclusions are as the following:

- The results indicate formation and stabilization of copper and nickel nanoparticle using synthesized cationic surfactants.
- By increasing the hydrophobic chain length of the synthesized cationic surfactants, the stability of prepared CuNPs and NiNPs increase.
- The antimicrobial activities of the compounds toward bacteria and fungi were high compared to the drug used.
- The antimicrobial and anti-fungal activity depended on the chemical structure of the synthesized surfactants and their nanostructure.
- The copper nanoparticles of the stabilized surfactants increase their biological activity more than nickel nanoparticles.

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