

## Investigation of Novel Mono Quaternary Surface Active Phosphonium Derivatives and Their Metal Complexes as Biocides for Metal Working Petroleum Oils

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**Abstract:** In this study, the surface active phosphonium derivatives and their metal complexes were synthesized and their chemical structures were investigated by elemental analysis, FTIR,  $H^1$  NMR and mass spectroscopy. The surface parameters of these compounds were studied to evaluate their surface activity. The biocidal and fungicidal characters of the target compounds and their metal complexes were compared to each others and with another commercial biocides through their effect against some strains of bacteria and fungi which grow in some metal working oils.

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**Keyword:** Mono quaternary, metal complexes, metal working oils

### 1. Introduction

The cationic surfactants have a unique ability of adsorption at the interfaces due to their amphiphathic structure, which acquires them a good biocidal activity towards microorganisms.<sup>1</sup> Synthesis and antimicrobial activity of some cross linked copolymers with quaternary ammonium and phosphonium groups. The synthesis and antimicrobial activities of modified poly (glycidyl methacrylate-co-2-hydroxyethyl methacrylate) and tartaric acid polyamides derivatives with quaternary ammonium and phosphonium salts were described.<sup>2</sup> The tributyl phosphonium salt of the polyamide was more effective against both Gram-negative and Gram-positive bacteria than the triethyl ammonium and triphenyl phosphonium salts of the polyamide,<sup>3</sup> Novel phosphonium salts which displayed *in vitro* and *in vivo* cytotoxic activity against human ovarian cancer Cell Lines. Phosphonium salts are part of a class of lipophilic cationic molecules that accumulate preferentially in mitochondria and inhibit the growth of human and rodent carcinoma cells *in vitro* and in animal models.<sup>4</sup>

### Material and Methods:-

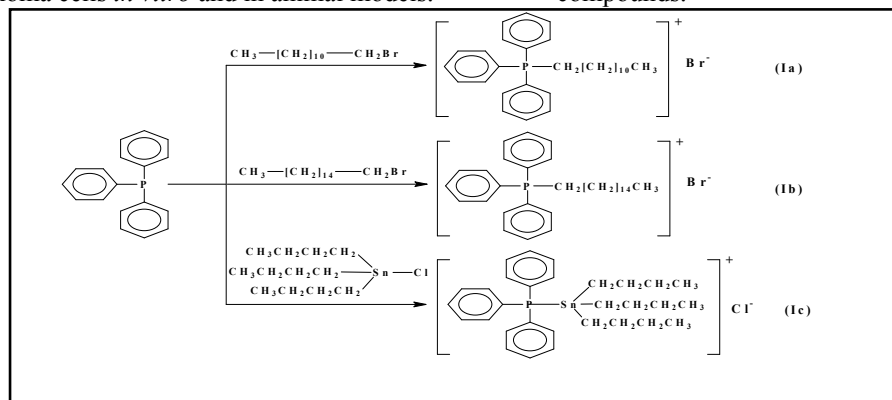
#### Materials

All of the used chemicals in this study were of analytical grade and supplied from international companies.

#### Methods

##### a. Synthesis of Mono-Quaternary Phosphonium Compounds (I<sub>a-c</sub>)

Equimolar amounts of triphenyl phosphine and dodecyl bromide, hexadecyl bromide and/or tributyl tin chloride were conducted to reflux in presence of acetonitrile as a solvent for 5 hours. Then, the reaction mixture was left over night to precipitate the produced monoquaternary products. The products were filtered under reduced pressure, and the residue was crystallized upon trituration with diisopropyl ether. The products were collected by vacuum filtration, washed with diisopropyl ether and dried<sup>5</sup>. Scheme (1) represents the chemical structures of the produced monoquaternary compounds.

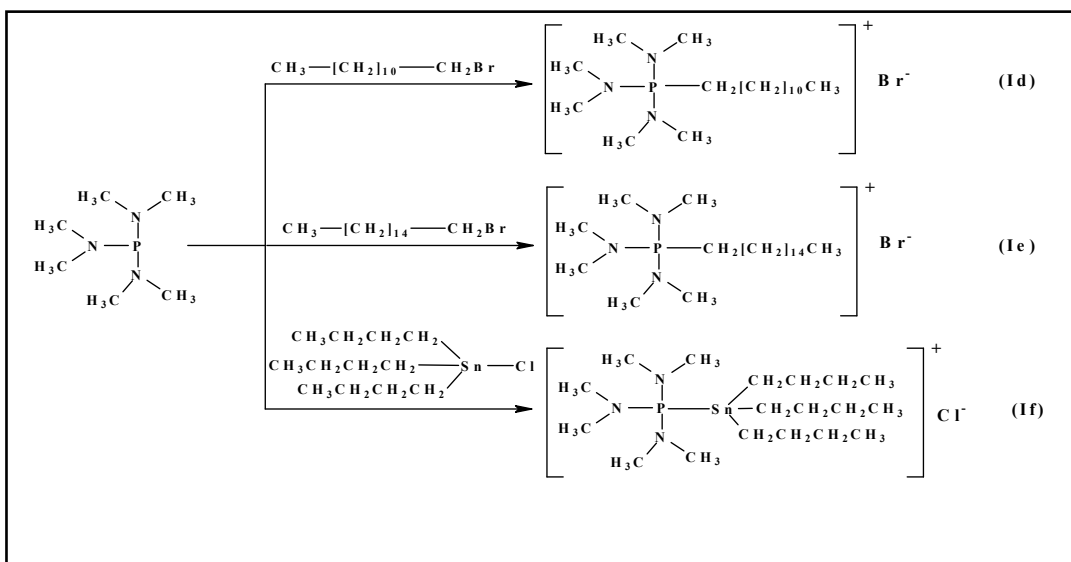


Scheme 1. Synthesis Of Triphenyl Mono-Quaternary Phosphonium Surfactants

### b. Synthesis of Mono-Quaternary Hexamethyl Phosphorus Triamide (I<sub>d-f</sub>)

Equimolar amounts of hexamethyl phosphorus triamide and different alkyl bromide derivatives namely: dodecyl bromide, hexadecyl bromide and/or tributyl tin chloride via mixing them and the mixture was slowly heated, with gently stirring to a temperature of 140-145°C at which temperature an exothermic reaction was evident. External heating was then discontinued and the temperature of the reaction

mixture was held at 140°C to 145°C for about 5 minutes by very moderate water-bath cooling. Heating was resumed, and stirring was continued for 2 hours at 140-145°C. The reaction mixture was then allowed to cool, this was dissolved in 100mL of hot dioxane and the resulting solution was cooled and treated with ether to precipitate the crystalline products. After repeated crystallization from dioxane and ether washes and vacuum drying,<sup>6</sup> Scheme (2).

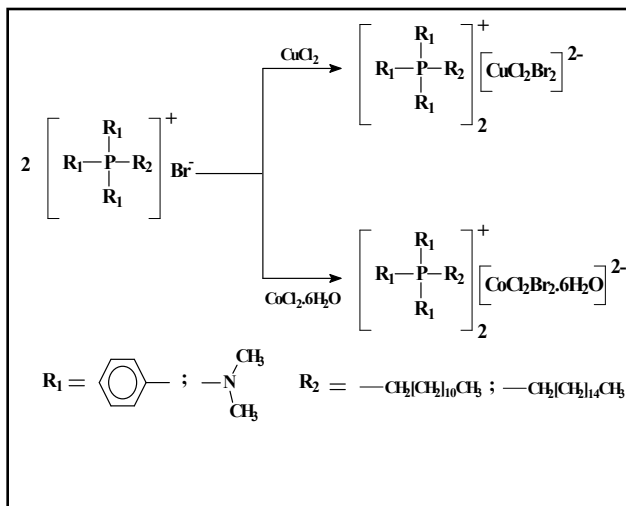


Scheme 2. Synthesis Of Mono-Quaternary Hexamethyl Phosphorus Triamide

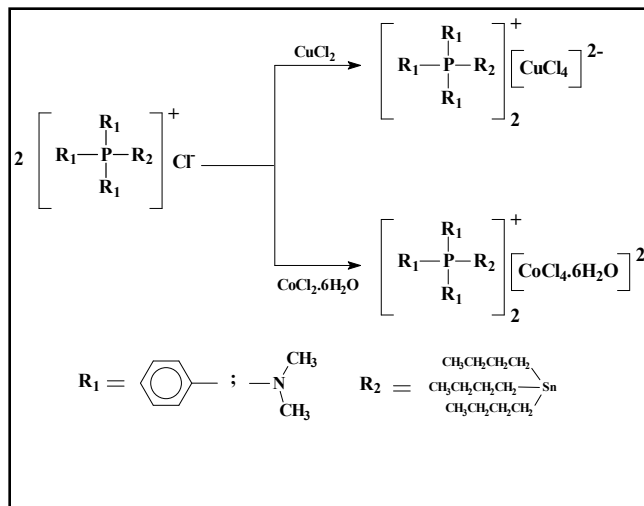
### c. Synthesis of Metal Complexes of Cu (II) and Co (II)

The synthesized monoquaternary compounds were complexed with metal chlorides namely: copper or cobalt in 2:1 molar ratio, respectively, in ethanol. The reaction mixtures were refluxed for 3 hours and

then allowed to precipitate overnight. The produced metal complexes were then filtered, washed twice with ethanol/petroleum ether mixture (50-50 vol.) and dried at 40°C under vacuum. Scheme (3, 4) represents the metal complexes of the monoquaternary compounds.<sup>7</sup>



Scheme 3. Synthesis of Metal Complex of Mono-Quaternary Compounds.



Scheme 4. Synthesis of Metal Complex of Mono-Quaternary Compounds.

**The analyses****a. Elemental Analyses**

Elemental analyses were performed using Vario-Elementar analyzer to determine the ration of carbon, hydrogen, nitrogen, phosphorus and halogen.

**b. Melting Point**

The melting points of the synthesized compounds were measured using Electrothermal Melting point apparatus.

**c. FTIR Spectra**

FTIR spectra were recorded using ATI Mattson Genesis Transformer FTIR.

**d. <sup>1</sup>H-NMR Spectroscopy**

<sup>1</sup>H-NMR spectra were measured using Varian Gemini-VX-3000 NMR spectrophotometer at 200MHz in DMSO-D<sub>6</sub> as a solvent and trimethyl silane as a reference.

**e. Mass Spectroscopy**

GC/MS spectra were measured using Hewlett Packard Spectrophotometer Model 5988A GC/MS.

**f. Atomic Absorption Spectroscopy (AAS)**

AAS were measured using Unicam-927 spectrophotometer.

**The measurements****a. Surface Tension Measurements**

Surface tension measurements were obtained using a K-6 Du-Nouy Tensiometer (Kruss GmbH). Freshly prepared aqueous amphiphiles solutions, with concentration range 0.1 to 0.0001 mol/l, were poured into a clean 30 mL petri dish with a mean diameter of 28mm. Apparent surface tensions were measured a minimum of 3 times at 25°C. The platinum ring was then removed, washed with diluted HCl followed by distilled water.<sup>8</sup>

**b. Interfacial Tension Measurements**

Interfacial tension measurements were made for surfactant-oil system at 25°C using surfactant solutions of concentration 0.1%, (the paraffin oil was (heavy, white) supplied from El-Gomhoria Chemicals Company, ADWIC). The interfacial tension value was taken after the ring separated from the interfacial surface between the two phases.<sup>9</sup>

**c. Emulsion Stability**

Emulsification power of the synthesized surfactants was measured by vigorous hand-shaking of 10 ml surfactant solution (0.1%) and 10 ml of the same paraffin oil described above for 5 minutes at 25°C. The emulsification power was expressed as the time required for separation of 9mL of pure water.<sup>9</sup>

**Biological Activity and Antimicrobial Studies**

The synthesized surfactants were screened for their antimicrobial activity against bacteria and fungi using agar well diffusion method.<sup>10</sup>

**a. Growing of Microorganisms**

The bacterial strains were cultured on nutrient medium, while the fungi strains were cultured on malt

medium. For bacteria, the broth media were incubated for 24 hrs. As for fungus, the broth media were incubated for approximately 48 hrs, with subsequent filtering of the culture through a thin layer of sterile Sintered Glass G2 to remove mycelia fragments before the solution containing the spores was used for inoculation.

**b. Measurements of Resistance and Susceptibility**

For preparation of discs and inoculation, 1.0 ml of inocula were added to 50 ml of agar media (40°C) and mixed. The agar was poured into 120 mm Petri dishes and allowed to cool to room temperature. Wells (6 mm in diameter) were cut in the agar plates using proper sterile tubes. Then, filled up to the surface of agar with 0.1 ml of the synthesized surfactants dissolved in DMF (1 mg/mL). The plates were left on a leveled surface, incubated for 24 hrs at 30°C for bacteria and 48 hrs for fungi and then the diameter of the inhibition zones were read. The inhibition zone formed by these compounds against the particular test bacterial strain determined the antibacterial activities of the synthetic compounds. The mean value obtained for three individual replicates was used to calculate the zone of growth inhibition of each sample. The results were compared with a similar run of commercial and applied biocide (Glokill 77) as an antibacterial and antifungal reference. Both antimicrobial activities were calculated as a mean of three replicates.

**c. Microorganisms**

The antimicrobial activities of the synthesized surfactants were tested against *Pseudomonas aeruginosa*, *Staphylococcus aureus*, While the fungicidal activities were tested against *Aspergillus flavus* and *Candida albicans*.

**Evaluation of the Synthesized Cationic Surfactants as Biocides for Metal-Working Oils**

The selected cationic surfactants were dissolved in imported naphthenic base oil [MVIN 40]with ratio1:3,i.e.25% then mixed with neutral base oil 140/160 produced from Amerya refinery,

**a. Preparation of the Metal Working Oil Formulation**

Metal working oil formulation was prepared by blending 77% wt. of neutral base oil 140/160 produced from Amerya refinery, 20% wt of commercial imported emulsifire EM 3154, which is the recommended dose 3% of each of the dissolved selected surfactants ( $I_a$ ,  $I_c$  &  $I_f$ ).

**b. Determination of Thermal Stability of Water Mix Metal-Working Fluids**

The thermal stability of the metal-working oil formulation in presence of the selected synthesized surfactants number ( $I_a$ ,  $I_c$ ,  $I_f$  and  $II_c$ ) were studied by applying the standard test method.<sup>11</sup>

This method covers the determination of the thermal stability of water mix metal-working fluids over the range of temperatures (0°C - 50°C) at which

the fluids would normally be stored. The method describes the tests of high temperature stability and low temperature stability.

#### c. Determination of Stability of Water Mix Metal-Working Oil Fluid

The determination of stability of water mix metal-working oil formulation in presence of the selected synthesized surfactants I<sub>a</sub>, I<sub>c</sub> & I<sub>f</sub> were studied by applying the standard test method.<sup>12</sup>

This method is accordingly designed to assess the stability of water mix metal working fluids used in the form of aqueous dilutions.

#### d. Determination of Frothing Characteristics of Water Mix Metal-Working Fluids

The determination of frothing characteristics of water mix metal-working oil formulation in presence of the selected synthesized surfactants I<sub>a</sub>, I<sub>c</sub>, I<sub>f</sub> and I<sub>e</sub> were studied by applying the standard test method.<sup>13</sup> This method assesses the frothing characteristics of water mix metal working fluids used in the form of aqueous dilutions.

#### e. Determination of Iron Corrosion Characteristics of Petroleum Products

Water mixed metal working fluids which are used in the form of aqueous dilutions should not readily permit corrosion of equipment with which they come into contact. This method is accordingly designed to determine the iron corrosion characteristics of mix metal-working oil formulation in presence of the selected synthesized surfactants I<sub>a</sub>,

I<sub>c</sub> and I<sub>f</sub> were studied by applying the standard test method.<sup>14</sup>

#### f. Microbiological Test for Soluble Metal Working Oil with the Synthesized Selected Cationic Surfactants

##### Procedure

- 1- 1 ml of emulsion was diluted with 100 ml sterilized water.
- 2- The solution was then filtered through a clean and sterilized buncher stainless steel through 0.45 micro membranes for total bacterial plate count and 0.75 micro membrane for molds and yeast count
- 3- The membrane was then incubated on beef extract peptone agar for bacterial growth and wart agar for molds and yeast growth.
- 4- The Petri dishes were then incubated at 35°C for bacteria (1 day) and at 25°C for molds and yeast (3 days)

After the incubation period has ended, the colonies were then counted and reported.<sup>15</sup>

### 3. Results and Discussion:-

#### Structure

##### a. Elemental Analyses

The ratio between the found and calculation ratio were conformed and proved that the synthesized compounds are highly pure and have no impurities ( Table 1).

**Table 1: Elemental Analyses of the Synthesized Compounds**

Abb.	M.wt	Carbon		Hydrogen		Nitrogen		Phosphorus		Bromine		Chlorine		Stannous	
		Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
I <sub>a</sub>		70.46	70.43	7.82	7.80	---	---	6.06	6.02	15.63	15.59	---	---	---	---
I <sub>b</sub>	510.87	71.97	71.93	8.46	8.42	---	---	5.46	5.44	14.09	14.05	---	---	---	---
I <sub>c</sub>	566.87	61.30	61.23	7.15	7.13	---	---	5.27	5.26	---	---	6.04	6.01	20.21	20.19
I <sub>d</sub>	587.18	52.44	52.42	10.44	10.42	10.19	10.18	7.51	7.49	19.39	19.37	---	---	---	---
I <sub>e</sub>	411.87	56.42	56.39	10.90	10.87	8.97	8.95	6.61	6.59	17.07	17.05	---	---	---	---
I <sub>f</sub>	467.87	44.24	44.21	9.21	9.19	8.60	8.58	6.34	6.32	---	---	7.27	7.24	24.31	24.29
	488.18														

**Table 2: Melting Points of the Synthesized Compounds**

Compound	Molecular weight, gm/mole	Melting point, °C (±1 °C)
I <sub>a</sub>	510.87	128
I <sub>b</sub>	566.87	139
I <sub>c</sub>	587.18	146
I <sub>d</sub>	411.87	103
I <sub>e</sub>	467.87	116
I <sub>f</sub>	488.18	125

**b. Melting Point**

The melting point measurements of the synthesized compounds showed sharp melting point values. That indicates the purity of these compounds, Table (2).

**c. FTIR Spectroscopy**

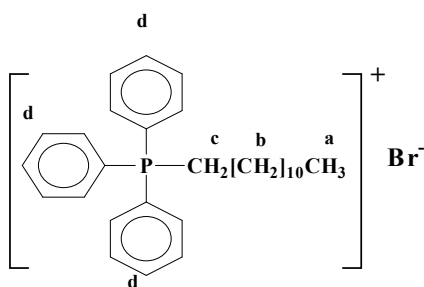
The FTIR spectroscopy of the synthesized cationic surface active agents (I<sub>a</sub>, I<sub>b</sub>, I<sub>c</sub>, I<sub>d</sub>, I<sub>e</sub> and I<sub>f</sub>) showed the characteristic absorption bands at their characteristic values (cm<sup>-1</sup>), Table (3)

**Table 3 : FTIR Spectral Bands of the Synthesized Compounds**

Surfactant	CH <sub>3</sub> (cm <sup>-1</sup> ), Sym., Assym.	CH <sub>2</sub> (cm <sup>-1</sup> ), Sym., Assym.	CH-aromatic (cm <sup>-1</sup> )	P-CH <sub>2</sub> (cm <sup>-1</sup> )	P-Ph (cm <sup>-1</sup> )
I <sub>a</sub>	2980, 2918	2851, 2848	873	1435	1187
I <sub>b</sub>	2942, 2922	2851, 2840	741	1469	1177
I <sub>c</sub>	2930, 2918	2856, 2845	846	---	1168
I <sub>d</sub>	2925, 2917	2848, 2775	---	1465	---
I <sub>e</sub>	2930, 2918	2849, 2792	---	1468	---
I <sub>f</sub>	2922, 2915	2844, 2786	---	---	---

**d. H<sup>1</sup>NMR Spectroscopy**

Compound I<sub>a</sub> showed the following signals: at 0.746-0.938ppm (triplet, 3H, **a** protons); at 1.028-1.308ppm (multiple, 20H, **b** protons); at 2.423-2.615ppm (triplet, 2H, **c** protons) and at 7.585-8.006ppm (multiple, 15H, **d** protons).

**b. Mass Spectroscopy**

Mass spectra of synthesized cationic surfactants was in accordance with the expected structure figure showed the fragmentation spectra of the synthesized compound I<sub>a</sub> showed The molecular ion peak appeared at 511 While, the base peak appeared at 77. and showed fragments at m/e = 51, 52, 54, 55, 56, 107, 108, and 263.

**c. Atomic Absorption Spectroscopy**

Table 4 shows the ratio of the transition metals in the synthesized metal complexes. The ratio showed that the complex is formed in the ratio of two ligands to one metal ion. The expected geometrical structure of the formed complexes is tetrahedron structure.

**Table 4 : Transition Metals Ratio of the Synthesized Complexes**

Abb.	Copper complex			Cobalt complex		
	M.Wt	Metal (%)		M.Wt	Metal (%)	
		Calc.	Found		Calc.	Found
I <sub>a</sub>	1156.29	5.49	5.48	1259.67	4.68	4.66
I <sub>b</sub>	1268.29	5.01	5.00	1371.67	4.30	4.28
I <sub>c</sub>	1308.91	4.86	4.86	1412.29	4.17	4.15
I <sub>d</sub>	958.29	6.63	6.62	1061.67	5.55	5.54
I <sub>e</sub>	1070.29	5.94	5.93	1173.67	5.02	5.01
I <sub>f</sub>	1110.91	5.72	5.71	1214.29	4.85	4.83

**Surface Properties****a. Surface and Interfacial Tension**

Surface active agent molecules of the surfactant are characterized by two features. Firstly, the presence of nonpolar part in their chemical structures, which is called the hydrophobic part or chain. Secondly, the presence of polar part either cationic (positively charged), anionic (negatively charged) or nonionic. These features play a vital role in the solubility of these molecules in both polar and nonpolar solvents. The ability towards solubility in both polar and

nonpolar solvents is called the amphipathic character and the surfactant molecule, hence being an amphiphiles.

The unique property of the surfactant molecules is their tendency towards adsorption at the interface, air-liquid, liquid-liquid or solid-liquid interfaces. Hence, depression in the surface tension is expected to occur for their solutions.

Figures (1-6) represent the variation of the surface tension of the synthesized monoquaternary triphenyl phosphonium and hexamethyl phosphonium

triamide surfactants I<sub>a</sub>, I<sub>b</sub>, I<sub>c</sub>, I<sub>d</sub>, I<sub>e</sub> and I<sub>f</sub> against the concentration at 25°C and also their metal complexes.

It is clear from Figures (1- 6) that the surface tension values are strongly dependant on the length of the hydrophobic chains attached to the surfactant molecules. Increasing the surfactant concentration decreases the surface tension values considerably till it reaches the critical micelle concentration (CMC). Increasing the hydrophobic chain length of the synthesized monoquatarnary triphenyl phosphonium and triamide compounds (I<sub>a</sub>, I<sub>b</sub> and I<sub>d</sub>, I<sub>e</sub>) from 12 to 16 methylene groups decreases the surface tension considerably.

The gradual decrease in the surface tension happens due to increasing the adsorption tendency of these molecules at the air-water interface. The adsorption tendency is increased due to increasing the repulsion force between the nonpolar hydrophobic chains and the polar solvent (H<sub>2</sub>O). This repulsion increases from C<sub>12</sub> chain to C<sub>16</sub> chain. When the adsorption of the surfactant molecules is at the interface, the hydrogen bonds between the water molecules is broken, hence, the surface tension decreases<sup>16</sup>. On comparison between the triphenyl phosphonium and hexamethyl phosphonium triamides. Triphenyl phosphonium monoquatarnary derivatives show lower surface tension values compared with hexamethyl phosphonium triamide derivatives containing similar hydrophobic chain length (either dodecyl- or hexadecyl)<sup>17</sup>. That is due to the presence of the phenyl groups in the surfactant molecules. The phenyl groups are characterized by high hydrophobicity due to the presence of several double bonds which increases the hydrophobicity of triphenyl phosphonium derivatives. Hence, their surface tension values decrease considerably. On the

other hand, hexamethyl phosphonium triamide derivatives are characterized by more hydrophilic groups which increase their hydrophilicity; hence their surface tension values increase.

The tributyl tin derivatives show the highest surface tension values throughout the synthesized compounds (I<sub>c</sub>, I<sub>f</sub>). That is due to the short chain length of their hydrophobic chain; in addition, the branching decreases the surface activity.

On complexation of the synthesized triphenyl phosphonium mono-quatarnary with different transition metals, the surface tension values were changed remarkably<sup>18</sup>. Cobalt and copper ion complexes of the cationic surfactants show high decreasing tendency on the surface tension values rather than the parent cationic surfactants itself. This behavior could be attributed to the large hydrophobic chain contents in the complex molecules. The high hydrophobic content increases the hydrophobicity of the complex molecules, subsequently increases the repulsion forces between them and the water phase. Hence, the complex molecules migrate to the air-water interface, which leads to a high suppression in the surface tension.

The interfacial tension of the oil / surfactant systems at (25°C) was measured for synthesized cationic surfactants and their metal complexes. It is clear from the data listed in tables (5,6) that the synthesized cationic surfactants (I<sub>a-f</sub>) and their metal complexes have good interfacial tension values against paraffin oil. The hydrophobic chain length of these surfactants was not affected by the interfacial tension values. Also, the lower values of the interfacial tension values indicate the ability of using these surfactants in several applications as biocides.

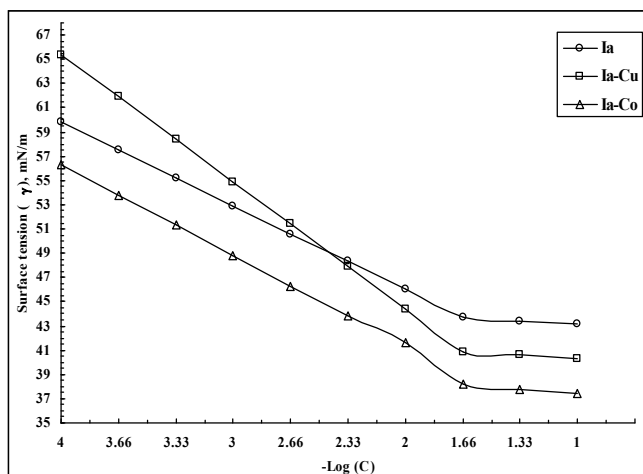


Figure 1. Relation between surface tension and  $-\log$  conc. Of the synthesized compounds Ia at 25°

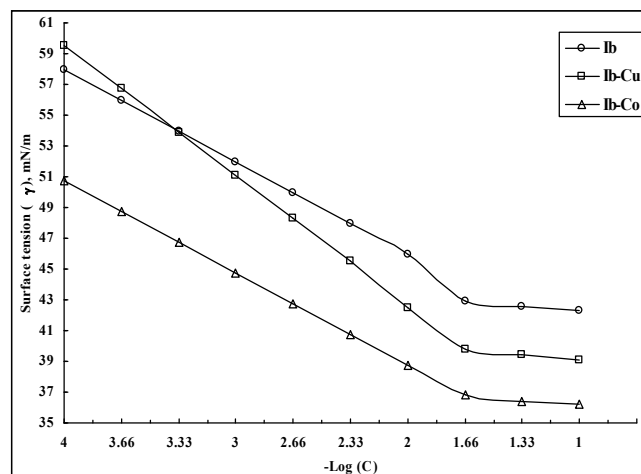


Figure 2. Relation between surface tension and  $-\log$  conc. of the synthesized compounds Ib at 25°C

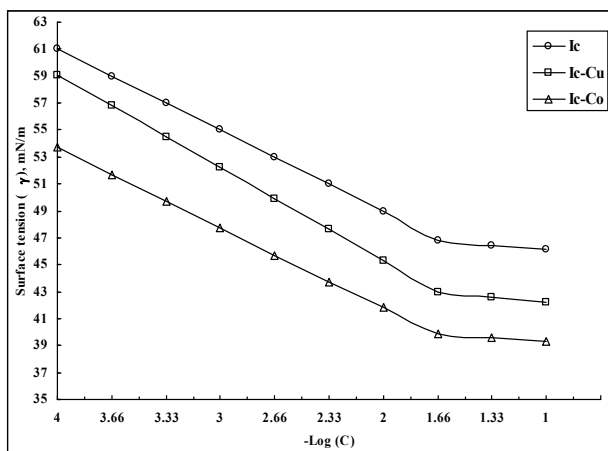


Figure 3. Relation between surface tension and  $-\log$  conc. of the synthesized compounds Ic at 25°C

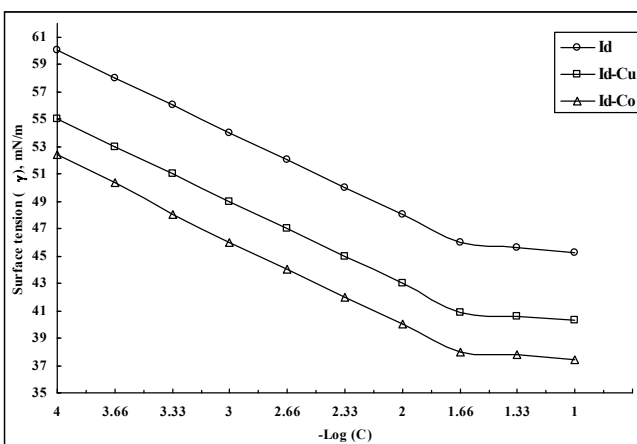


Figure 4. Relation between surface tension and  $-\log$  conc. of the synthesized compounds Id at 25°C

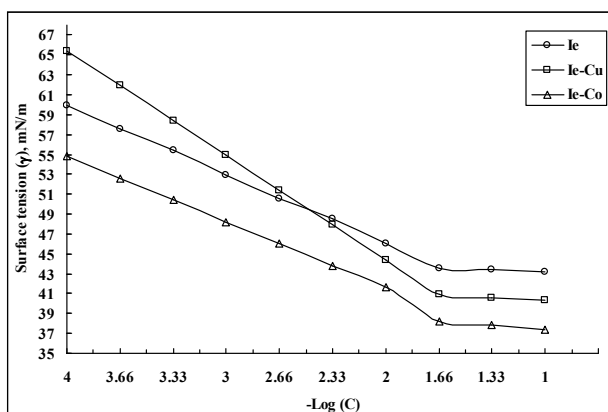


Figure 5. Relation between surface tension and  $-\log$  conc. of the synthesized compounds Ie at 25°C

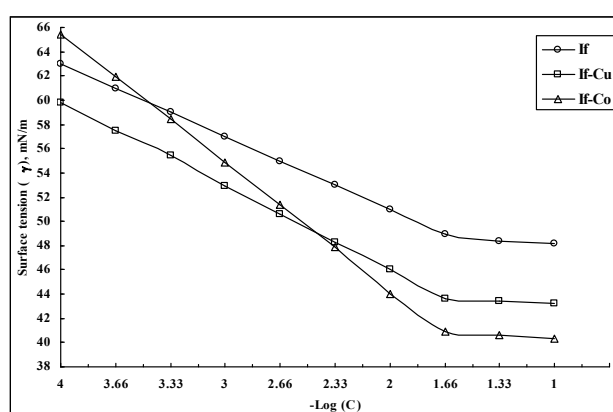


Figure 6. Relation between surface tension and  $-\log$  conc. of the synthesized compounds If at 25°C

### b. Critical Micelle Concentration (CMC)

The surface tension vs.  $-\log$  concentration profile show that the variation of surface tension has two behaviors. At lower concentrations, ( $\gamma$ ) were increased considerably, while at higher concentrations, ( $\gamma$ ) were stay almost constant. The intercept between the two regions occurs at sharp concentration point called critical micelle concentration (CMC).

At the CMC, there is equilibrium between the individual adsorbed molecules and the aggregated molecules in the formed micelles. (Table 5) represents the CMC values of the synthesized monoquatary triphenyl phosphonium and hexamethyl phosphonium triamide surfactants at 25°C. It is clear from the CMC

values that the synthesized surfactants are characterized by low CMC values compared with the ordinary homologues. Also, increasing the hydrophobic chain lengths from 12 to 16 methylene groups decreases the CMC remarkably.

Table 6 showed the CMC values of copper and cobalt metal complexes of the synthesized surfactants at 25°C. It is clear that the metal complexation of the synthesized cationic surfactants decrease their critical micelle concentration values compared to their parent cationic surfactants. This can be attributed to the higher hydrophobic character of these metal complexes due to the participation of two surfactant molecules in one metal complex molecule.

**Table 5: Surface Tension, Critical Micelle Concentrations and Interfacial Tension of the Synthesized Cationic Surfactants at 25°C**

Surfactant	Surface Tension of 0.1% solution mN/m	Critical Micelle Concentrations CMC (mMole/L)	Interfacial Tension of 0.1% solution mN/m
I <sub>a</sub>	43	21.87	7
I <sub>b</sub>	42	20.89	4
I <sub>c</sub>	46	26.90	5
I <sub>d</sub>	45	24.37	11
I <sub>e</sub>	43	21.43	9
I <sub>f</sub>	48	25.70	12

**Table 6: Surface Tension, Critical Micelle Concentrations and Interfacial Tension of the Synthesized Metal Complexes Surfactants at 25°C**

Surfactant	Surface Tension of 0.1% solution mN/m		Critical Micelle Concentrations CMC (mMole/L)		Interfacial Tension of 0.1% solution mN/m	
	Copper Complex	Cobalt Complex	Copper Complex	Cobalt Complex	Copper Complex	Cobalt Complex
I <sub>a</sub>	40	37	20.63	19.68	9	10
I <sub>b</sub>	39	36	19.40	19.10	5	7
I <sub>c</sub>	42	39	23.30	21.17	6	8
I <sub>d</sub>	40	37	21.27	20.87	12	13
I <sub>e</sub>	40	37	20.20	19.91	11	10
I <sub>f</sub>	43	40	23.70	21.21	12	13

The synthesized surfactants produce stable emulsions formed from paraffin oil and water in presence of 0.1% surfactant concentration. The stability is ranged between 780 seconds and 100 seconds depending on the chemical structures of the used surfactants in the emulsification process (Table 7).

On complexation of the synthesized surfactants with cobalt or copper ions the stability of the formed emulsions increase considerably (Table 7).

The stabilization of the formed emulsion depends on the ability of these compounds to locate at

the interfaces between the two different phases (oil/water). The hydrophobic contents of the compounds increase by metal complexation introducing charged centers in their chemical structures which increases their tendency towards the location at the interfaces. Correspondingly, the interaction between the different phases decreases and facilitates their reactivity. Hence, the stability of the metallo micellar cationic surfactants increase considerably.

**Table 7: Emulsification Power of the Synthesized Cationic Surfactants and their metal complexes at 25°C**

Surfactants	Emulsification power, sec.	Emulsification power, sec.	
		Copper complex	Cobalt complex
I <sub>a</sub>	450	840	660
I <sub>b</sub>	780	840	1340
I <sub>c</sub>	203	300	360
I <sub>d</sub>	100	240	300
I <sub>e</sub>	203	210	240
I <sub>f</sub>	300	660	780

## Surface Parameters

### a. Effectiveness ( $\pi_{cmc}$ ) and Efficiency ( $P_{c20}$ )

The effectiveness is a useful factor in comparison between different surfactants within similar group. Another factor can be considered in surface activity study which determines the surface activity of the surface active agents. That factor can be determines the most surface active compound through different types of surfactants and called efficiency ( $P_{c20}$ ). Decreasing

the efficiency values to lower concentrations indicates the higher surface activity of the surfactants and vice versa. (Table 8) shows that the synthesized mono-quaternary triphenyl phosphonium and hexamethyl phosphonium triamide cationic surfactants are characterized by higher effectiveness and lower efficiency values. That represents their tendency towards adsorption at the interfaces (air-water) and also micellization.



Generally, the effectiveness and efficiency values showed that the synthesized compounds have good ability towards adsorption at the different interfaces<sup>7</sup>. The effectiveness values of the synthesized metal complexes showed a slight depression in most complexes than their parent triphenyl phosphonium and hexamethyl phosphonium triamide compounds, (Tables

8). The lower depression in  $\pi_{cmc}$  was occurred only in the solutions of complexes formed from parent triphenyl phosphonium surfactants with low  $\pi_{cmc}$  values. In addition, the efficiency values ( $Pc_{20}$ ) of metal complexes were considerably decreased than their parent compounds.

**Table 8 : Effectiveness and Efficiency of the Synthesized Cationic Surfactants and their metal complexes at 25°C**

Surfactants	Effectiveness, $\pi_{cmc}$ (mN/m)	Efficiency, $Pc_{20}$ (mMole/L)	Effectiveness, $\pi_{cmc}$ (mN/m)		Efficiency, $Pc_{20}$ (mMole/L)	
			Copper Complex	Cobalt Complex	Copper Complex	Cobalt Complex
I <sub>a</sub>	28.1	2.19	26.7	21.3	0.79	0.58
I <sub>b</sub>	26.5	8.31	25.4	19.9	0.16	0.16
I <sub>c</sub>	25.9	1.23	24.4	23.3	0.32	0.83
I <sub>d</sub>	24.8	3.55	23.3	22.3	1	3.8
I <sub>e</sub>	23.80	8.31	22.4	21.4	0.83	2.1
I <sub>f</sub>	26.80	2.7	25.2	24.2	1.3	1

### b. Maximum Surface Excess ( $\Gamma_{max}$ )

The mathematical analysis of the maximum surface excess definition reveals that  $\Gamma_{max}$  is proportional directly to  $\partial\gamma/d\log C$ . That indicates the increasing of  $\partial\gamma/d\log C$  increases the surface concentration, hence;  $\partial\gamma/d\log C$  is called the surface pressure. The surface pressure increased by increasing the difference between the two surface tension values at very low concentration intervals. That is directly related to the ability of the surfactant molecules towards adsorption at the air-water interfaces. Increasing the hydrophobic chain lengths increases their surface pressure due to the interaction with the aqueous medium. Increasing the hydrophobic chain length increases their hydrophobicity, i.e., their nonpolar character. That leads to pump the surfactant molecules towards the interface and  $\Gamma_{max}$  values increases considerably.<sup>7</sup>

Table 9 represents the maximum surface excess values of the synthesized mono- quaternary phosphonium and hexamethyl phosphonium triamide derivatives surfactants at 25°C were increased by increasing the hydrophobic chain lengths from 12 to 16 methylene groups.

The maximum surface excess of the synthesized metal complexes were increased with complexation than the parent cationics. That was coincident with the higher surface tension depression of these complexes. The main conclusion explaining that is: the increase in  $\Gamma_{max}$  is due to increasing the tendency of these complexes towards adsorption at the interface as a result of increasing their surface pressure. The surface pressure increased due to increasing the hydrophobicity of the molecules by complexation, (Table 9).

**Table 9 : Maximum Surface Excess of the Synthesized Cationic Surfactants and their metal complexes at 25°C**

Surfactants	Maximum surface excess, $\Gamma_{max}$ , mol.cm <sup>-2</sup> .K <sup>-1</sup> 10 <sup>-11</sup>	Maximum surface excess, $\Gamma_{max}$ , mol.cm <sup>-2</sup> .K <sup>-1</sup> 10 <sup>-11</sup>	
		Copper complex	Cobalt complex
I <sub>a</sub>	1.77	1.97	2.05
I <sub>b</sub>	1.85	1.87	1.76
I <sub>c</sub>	1.65	1.65	1.90
I <sub>d</sub>	1.82	1.87	2.24
I <sub>e</sub>	1.98	2.06	2.13
I <sub>f</sub>	1.85	1.98	2.13

### c. Minimum Surface Area ( $A_{min}$ )

The area occupied by each molecule at the interface is influenced by several factors including the polar groups in the molecules, hydrophobic chain length and geometrical structure of the molecules. The synthesized hexamethyl triamide derivatives show

lower  $A_{min}$  than the triphenyl phosphine derivatives with similar hydrophobic chain length, (Table 10).

Calculation of the minimum surface area occupied by each metal complex molecule at the interface show gradual decrease than the parent cationic phosphonium compounds. That can be attributed to the geometrical structure of these metal

complexes and the restriction of motion occurred for the different components in the tetrahedron structure. The metal complexation decreases the point of attachment of the molecules at the interface, which decreases  $A_{\min}$  remarkably. In addition, the electronegativity of the transition metals strongly attracts the phosphonium ions and correspondingly decrease  $A_{\min}$ , (Table 10).

Generally, cobalt complexes show lower  $A_{\min}$  than copper complexes. This can be explained throughout the higher electronegativity of  $\text{Co}^{++}$  than  $\text{Cu}^{++}$ . Hence, the ligands are attracted strongly to  $\text{Co}^{++}$  ions than to  $\text{Cu}^{++}$  ions and subsequently  $A_{\min}$  decreases remarkably in the former ones.<sup>1</sup>

**Table 10 : Minimum Surface Area of the Synthesized Cationic Surfactants and their metal complexes at 25°C**

Surfactants	Minimum surface area, $A_{\min}$ , nm <sup>2</sup>	Minimum surface area, $A_{\min}$ , nm <sup>2</sup>	
		Copper complex	Cobalt complex
I <sub>a</sub>	9.4	8.41	8.11
I <sub>b</sub>	8.97	8.55	8.42
I <sub>c</sub>	10.06	9.16	8.65
I <sub>d</sub>	9.1	9.00	8.75
I <sub>e</sub>	8.62	8.44	8.00
I <sub>f</sub>	8.96	8.06	7.75

### Thermodynamic of Adsorption and Micellization

The thermodynamic functions of adsorption and micellization can determine easily the tendency of surfactant molecules in their solutions towards the two mentioned processes. The most useful thermodynamic functions are the standard free energy of adsorption and micellization ( $\Delta G_{\text{ads}}$ ,  $\Delta G_{\text{mic}}$ ). These factors tell the spontaneous and preferability of each process.

Tables (11) represent both  $\Delta G_{\text{ads}}$  and  $\Delta G_{\text{mic}}$  of the synthesized surfactants and their metal complexes at 25°C. The results show that the values of standard free energies of micellization and adsorption are always negative. This indicates the spontaneous behavior of the two processes. Also, it appears that the values of

adsorption free energies are more negative than that of micellization. This indicates the slight tendency of the synthesized compounds towards adsorption than micellization. Increasing the tendency of surface active agents towards adsorption increases their fields of application in the interfacial applications. These applications are including emulsification, corrosion inhibition, biocides, phase transfer catalysis, cosmetic production, foaming agents and demulsifiers. On contrarily, increasing the tendency towards micellization increases their tendency towards bulk application. These are including solubilization, detergency, drugs delivery, polymerization and micellar reactors.

**Table 11: Free Energy Changes of Adsorption and Micellization of the Synthesized Cationic Surfactants and their metal complexes at 25°C**

Surfactants	Standard free energy, KJ.mol <sup>-1</sup>					
	Adsorption, $\Delta G_{\text{ads}}$	Micellization, $\Delta G_{\text{mic}}$	Adsorption, $\Delta G_{\text{ads}}$		Micellization, $\Delta G_{\text{mic}}$	
			Copper Complex	Cobalt Complex	Copper Complex	Cobalt Complex
I <sub>a</sub>	-11.059	-9.467	-10.933	-10.873	-9.581	-9.638
I <sub>b</sub>	-10.142	-9.581	-11.059	-10.988	-9.938	-9.695
I <sub>c</sub>	-10.522	-8.953	-10.642	-10.737	-9.296	-9.524
I <sub>d</sub>	-10.595	-9.296	-10.841	-10.808	-9.524	-9.581
I <sub>e</sub>	-10.976	-9.512	-11.00	-10.938	-9.638	-9.695
I <sub>f</sub>	-10.131	-9.353	-10.282	-10.467	-9.239	-9.524

### Biocidal Activity

#### a. Biocidal Activity and Structure

The biological activity of the synthesized cationic monoquatary triphenyl phosphonium and hexamethyl phosphonium triamide compounds against different bacterial strains (gram +ve and gram -ve) and fungi are listed in (Table 12).

The inhibition zone diameters in (Table 12) are ranged between 11 and 64 mm for the monoquatary

triphenyl phosphonium and hexamethyl phosphonium triamide compounds. The higher score was found for the compounds which contain shorter hydrophobic chain. On the other hand, longer hydrophobic chains exhibit low biocidal activities towards the targeted bacterial strains and fungi.

The monoquatary triphenyl phosphonium and hexamethyl triamide phosphonium derivatives of tributyl tin chloride (I<sub>c</sub> and I<sub>f</sub>) show the highest biocidal

activities towards both bacteria and fungi. This can be attributed to the potent influence of tin metal towards the bioreactions in the cellular system.

Generally, the biocidal activity of the monoquaternary derivatives increases in shorter hydrophobic chains and increases by minor values in case of triphenyl phosphonium derivatives.

**Table 12: Biocidal Activity of the Synthesized Mono-Quaternary Triphenyl Phosphonium and Hexamethyl Phosphonium Triamide Derivatives**

Compound	Inhibition zone diameter (mm/mg)			
	<i>Pseudomonas aeruginosa</i> (Gram -ve)	<i>Staphylococcus aureus</i> (Gram +ve)	<i>Aspergillus flavus</i> (Fungus)	<i>Candida albicans</i> (Fungus)
<b>Control</b>	0.0	0.0	0.0	0.0
<b>I<sub>a</sub></b>	20	19	16	16
<b>I<sub>b</sub></b>	13	13	13	15
<b>I<sub>c</sub></b>	40	64	25	30
<b>I<sub>d</sub></b>	15	19	0.0	16
<b>I<sub>e</sub></b>	16	15	11	16
<b>I<sub>f</sub></b>	21	28	17	24
<b>Reference*</b>	<b>46</b>	<b>49</b>	<b>31</b>	<b>21</b>

\* Glokill-77

Complexation of the synthesized triphenyl phosphonium and hexamethyl phosphonium triamide cationic surfactants by copper or cobalt ions increase their biocidal activity considerably against the tested bacteria (gram +ve and gram -ve) and fungi. The data in (Tables 13,14) shows increased trend in the biocidal activities of the metal complexes than their parent cationics. The type of metal ions plays an important role

in the activity of the different metal complexes. Generally, cobalt complexes of the cationic phosphonium surfactants show minor increase in the biocidal activity for both monoquaternary triphenyl phosphonium or hexamethyl phosphonium triamide derivatives towards the targeted bacterial strains and fungi compared with the copper complexes of the same cationics.

**Table 13 : Biocidal Activity of the Synthesized Cationic Triphenyl Phosphonium and Hexamethyl Phosphonium Triamide Copper Complexes**

complex	Inhibition zone diameter (mm/mg)			
	<i>Pseudomonas aeruginosa</i> (Gram -ve)	<i>Staphylococcus aureus</i> (Gram +ve)	<i>Aspergillus flavus</i> (Fungus)	<i>Candida albicans</i> (fungus)
<b>Control</b>	0.0	0.0	0.0	0.0
<b>I<sub>a</sub></b>	20	20	16	16
<b>I<sub>b</sub></b>	15	14	13	18
<b>I<sub>c</sub></b>	40	42	21	31
<b>I<sub>d</sub></b>	17	18	14	16
<b>I<sub>e</sub></b>	16	17	14	17
<b>I<sub>f</sub></b>	22	24	19	24

**Table 14 : Biocidal Activity of the Synthesized Cationic Triphenyl Phosphonium and Hexamethyl Phosphonium Triamide Cobalt Complexes**

Compound	Inhibition zone diameter (mm/mg)			
	<i>Pseudomonas aeruginosa</i> (Gram -ve)	<i>Staphylococcus aureus</i> (Gram +ve)	<i>Aspergillus flavus</i> (Fungus)	<i>Candida albicans</i> (fungus)
<b>Control</b>	0.0	0.0	0.0	0.0
<b>I<sub>a</sub></b>	21	20	17	18
<b>I<sub>b</sub></b>	15	17	14	18
<b>I<sub>c</sub></b>	42	60	11	30
<b>I<sub>d</sub></b>	16	19	13	16
<b>I<sub>e</sub></b>	24	24	16	22
<b>I<sub>f</sub></b>	40	56	25	38

### b. Biocidal Activity and Surface Properties

The Biocidal activity of the synthesized cationic triphenyl phosphonium and hexamethyl phosphonium triamide derivatives is strongly related to their surface activity. A deep sight in the values of maximum surface excess and the Biocidal activity reveals that increasing the  $\Gamma_{\max}$  values is conjugated by increasing the Biocidal activity. Also, decreasing the minimum surface area of the synthesized cationics increases the biocidal activity considerably.<sup>19</sup>

Increasing the negativity of the adsorption free energy changes of the synthesized cationic compounds is accompanied by increase in their Biocidal activity. The lowering in minimum surface area ( $A_{\min}$ ) and increasing of maximum surface excess ( $\Gamma_{\max}$ ) show increase of adsorbed molecules at the interface, hence, increase of adsorbed cationic surfactant molecules (biocide molecules) at the cellular membrane. Moreover, the high negativity of the standard free energies of adsorption confirms the strong adsorption of these molecules at the targeted membranes.

The increase in biocides density at the cellular membrane increases their potent activity for the tested bacteria and fungi. The more Biocidal activity of the copper and cobalt complexes of the synthesized cationics is attributed to the large maximum surface excess ( $\Gamma_{\max}$ ), low minimum surface area and high

depression in their  $\Delta G_{\text{ads}}$ . In conclusion, the Biocidal activity of the synthesized cationic triphenyl phosphonium and triamide phosphonium derivatives and their copper and cobalt complexes is controlled by the surface activity factor and also by the thermodynamic factor. Hence, the biocidal activity of these compounds is the result of the combination between the two mentioned factors.

### Evaluation of the Selected Synthesized Cationic Surfactants as Biocide for Water- Soluble Metal Working Oils,(Emulsion).

The water –soluble metal working oils are used as emulsions, so biocide must be added to prevent the growth of bacteria and fungi during the use of these emulsions. So the four selected synthesized cationic surfactants ( $I_a, I_c, I_e, I_f$ ) were evaluated as microbiological materials for emulsions of metal working oils. The results are listed in (Table 15) which indicates that the compound  $I_a$  &  $I_f$  are effective as antibacterial and antifungi for soluble metal working oils so:

- 1- Emulsions including each of  $I_a$  &  $I_f$  gave -ve results after 24 hrs or 48 hrs for bacterial, fungal and yeast counts similar to the commercial biocide Glokill 77.
- 2- On the other hand, emulsions including each of  $I_c$  failed in all counts results.

**Table 15: Results of Microbiological Tests for Water- Soluble Metal Working Emulsions Including the Selected Synthesized Cationic Surfactants ( $I_a, I_c$  &  $I_f$ ) Compared with Commercial Glokill 77**

Sample	Bacterial count colony/1ml sample		Fungal count colony/1ml sample	Yeast count colony/1ml sample
	24hrs	48hrs		
Emulsion without biocide	269	343	10	18
Emulsion with Glokill 77	- ve	- ve	- ve	- ve
Emulsion with $I_a$	- ve	- ve	- ve	- ve
Emulsion with $I_f$	- ve	- ve	- ve	- ve
Emulsion with $I_c$	36	58	10	12

**Table 16: Evaluation of the Synthesized Cationic Surfactants ( $I_a, I_c, I_f$ ) as Biocides Compared with Commercial Biocide (Glokill-77)**

Sample Test	Specification limit	$I_a$	$I_c$	$I_f$	$I_e$	Glokill-77
Blend stability, IP-311	Clear and homogeneous	Clear and homogeneous	Clear and homogeneous	Clear and homogeneous	Clear and homogeneous	Clear and homogeneous
Emulsification stability, IP-263 Oil separate Total separate material (max.)	Nil 0.5 mL	Nil 0.5 mL	Traces 0.5 mL	Nil 0.5 mL	Traces 0.5 mL	Nil 0.5 mL
Frothing characteristics, IP-312 0 min. 5 min.	Zero Zero	Zero Zero	Zero Zero	Zero Zero	Zero Zero	18 Zero
Corrosion test, IP-125	(0/0-0)	(0/0-0)	(0/0-0)	(0/0-0)	(0/1-1)	(0/0-0)
Alkalinity, pH at water dilution 20:1	8.5 (min.)	8.5	8.4	8.5	8.3	8.5

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