

Experimental Part

3. MATERIALS AND EXPERIMENTAL METHODS

3.1. Materials

The chemicals, which are used in this study, supplied from international companies and used as they are without more purification as shown in **Table (24)**.

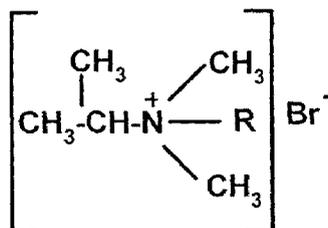
Table (24): List of origin of the used chemicals

No.	Material	Source
1	N,N-dimethyl isopropyl amine	Fluka, Germany
2	4- Dimethyl amino benzoic acid	Fluka, United Kingdom
3	1- Bromodecane	Fluka, France
4	1- Bromododecane	Fluka, France
5	1- Bromohexadecane	Fluka, France
6	Ethylene oxide	Merck, Germany.
7	Ethanol	Adwic, Egypt.
8	Hydrochloric acid	Panreac, Espana (Barcelona)
9	Potassium hydroxide	PHD
10	Isopropanol	Bio.Chem, Egypt.

3.2. Experimental techniques

3.2.1. Synthesis of surfactants

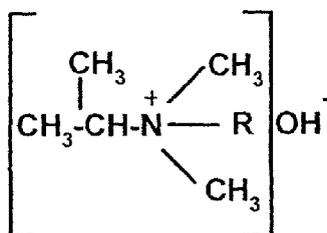
3.2.1.1. Cationic quaternary ammonium fatty alkyl bromide surfactants



R= CH₂(CH₂)₈CH₃ (decane), CH₂(CH₂)₁₀CH₃ (dodecane),
CH₂(CH₂)₁₄CH₃ (hexadecane).

A mixture of N,N-dimethylisopropylamine (one mole), the alkyl bromide (decyl, dodecyl and hexadecyl bromide)(one mole) in acetone was heated under reflux at 70 to 80 °C for 10 to 24 hours (depends on alkyl chain length). At the end of this period, products were purified by recrystallization three times in acetone and then washed with diethyl ether.

3.2.1.2. Cationic quaternary ammonium fatty alkyl hydroxide surfactants

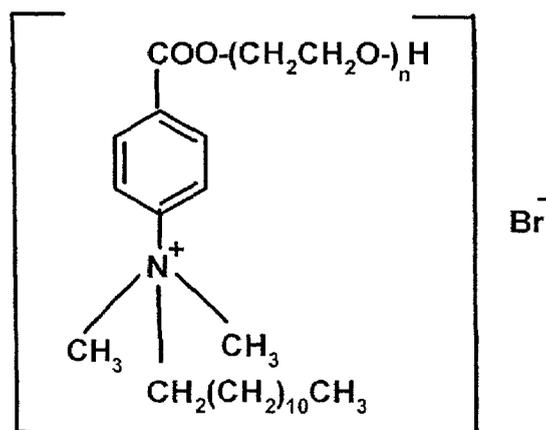


R= CH₂(CH₂)₈CH₃ (decane), CH₂(CH₂)₁₀CH₃ (dodecane),
CH₂(CH₂)₁₄CH₃ (hexadecane)

Potassium hydroxide pellets (one mole) was refluxed with N,N,N,N-alkyldimethylisopropylammonium bromide (one mole) in absolute ethanol. The resulting mixture was stirred and heated at 60-70 °C for three hours. The mixture was then cooled to give white precipitated solid (potassium bromide), which was collected on a filter paper and washed with cold ethanol. The

filtrate was concentrated, to give the corresponding N,N,N,N-alkyldimethylisopropylammonium hydroxide.

3.2.1.3. Ethoxylation of cationic quaternary ammonium fatty alkyl bromide surfactants



where, n about 54, 64, 74 and 84 units

Ethoxylated N,N,N,N-alkyldimethylammonium bromide benzoic acid was prepared by ethoxylation of N,N-dimethylaminobenzoic acid (one mole) inside the reaction reactor with 0.3 gm sodium metal as a catalyst and heated to 150-180 °C with continuous stirring while passing a stream of nitrogen gas through the system for 10 minutes to flush out air⁽¹³⁵⁾. The nitrogen stream was then replaced by ethylene oxide at a rate, which was regulated by monitoring the Hg-level of the manometer. The reaction was carried out at different intervals of time. The apparatus was then filled with nitrogen, cooled, and reaction reactor was weighed. The difference in weight indicated the amount of ethylene oxide which was consumed in the reaction. The mole numbers of ethylene oxide were calculated regarding to the weight difference^(136,137). The total number (n) of ethylene oxide groups with 54, 64, 74 and 84 units.

The obtained product was weighted, neutralized with HCl, dissolved in isopropanol, and then salted out with supersaturated NaCl solution. The

organic layer was then separated and the isopropanol was distilled off^(138, 139). The obtained ethoxylated product appeared as a brown viscous liquid appearance. Then, fatty alkyl bromide (dodecyl bromide) (one mole) was refluxed with ethoxylated of N,N-dimethylaminobenzoic acid (one mole) in acetone at 70 to 80 °C for 12 hours to give the corresponding product. The products were purified by recrystallization three times in ethanol, and then were washed with diethyl ether.

3.3. Structural confirmation of the prepared surfactants

The chemical structures of the prepared surfactants were confirmed by:

1. FT-IR spectra using ATI Mattsonm Infinity series TM, Bench top 961 controlled by Win First TM V2.01 software. (Egyptian Petroleum Research Institute).
2. ¹HNMR was measured in DMSO-d₆ by Spect Varian, GEMINI 200(1H 300 MHz). (Science Faculty, Cairo University).

3.4. Preparation of both surface tension and specific conductance solutions

The water was distilled twice and bathed through a column of mixed ion exchange resin (cation and anion), directly before using it for preparation or dilution. All prepared compounds were dried in vacuum at room temperature for at least 48 hours before used.

Prepare 50 ml of 0.1M from of the prepared surfactants, which were done by weighting the necessary amount of the sample and dissolved it in appropriate amount of water. The other concentration of the sample solutions were prepared by appropriate dilution of the 0.1M solution. It proceeds from one solution to the next by rinsing the cell with a few ml of the solution to be tested. The aggressive solution (1M HCl) was prepared by dilution of an analytical reagent grade of hydrochloric acid (37 %) with bi-distilled water.

The concentrations range which used in surface tension and conductance measurements from 8×10^{-4} to 1×10^{-1} M in bi-distilled water.

3.5. The surface tension measurements

Surface tension was measured on Tensiometer-K6 processor (Krüss Company, Germany) using the ring method. All the measurements were performed at 30 °C. The surface tension of pure water was initially obtained for each experiment for instrument calibration and determination of the water purity. Between the measurement runs, the ring was initially cleaned with pure water, then acetone. In each experiment, the surface tension of pure water was subtracted from the value of surfactant solutions. The apparent surface tension was measured 5 times for each sample within 2 minute interval between each reading ⁽¹⁴⁰⁾. CMC of the prepared surfactant was determined by the method adopted by Larinov ⁽¹⁴¹⁾. In this method, the surface tension (γ) of the surfactants solution at 25 °C was plotted against the logarithm of the solute concentration ($\log C$). The CMC values were determined from the abrupt change in the slope of (γ) versus ($\log C$) plots. Micelles of surfactants are formed in bulk aqueous solution above a given concentration for each surfactants and this concentration known as the critical micelle concentration (CMC) ⁽¹⁴²⁾.

3.6. Conductance measurements

Conductivity of solutions was measured using CRISON Conductivimeter 522, INSTRUMENTS, S. A. Barcelona Spain (series C-522, No. 8844, Volts 220, Amp. 0.1, and Hz 50).

Conductivity was measured with a cell consists of two platinum electrodes at a fixed distance apart. These electrodes were coated with finely divided electrodeposited platinum black. The ratio L/A is a property of the cell and was called the cell constant (where L is distance length between two platinum

electrodes and A is the surface area of one platinum electrodes). The resistance was measured with an alternating current to minimize electrolysis. The cell constant was not measured geometrically but by measuring the resistance of a sample solution of known conductivity, usually potassium chloride.

Immerse the conductance cell in a 50 ml beaker, filled with the appropriate solution. The electrodes must be completely covered by solution, to make sure there are no air bubbles at the electrode.

Measurements were done on the most dilute solution firstly in order to minimize errors due to imperfect rising and adsorption of ions on the electrodes. Then, repeat the series of the conductance measurements with tested solutions. After we had finished, rinse the cell with distilled water (as it was received) and return bridge and cell to stockroom.

All measurements were done in closed system at 30 °C in deionized water.

The temperature of the solution was maintained constant by circulating the cell compartment with water at proper temperature from water bath; it was controlled to ± 1 °C.

3.7. The Procedure of corrosion inhibition measurements

3.7.1. Weight loss measurements

Prior to all measurements were polished with different emery paper up to 1200 grade, washed thoroughly with bi-distilled water then degreased with acetone and dried at room temperature before use. Weight loss measurements were carried out in glass cell. The solution volume is 150 cm³. The steel specimens used have a rectangular form (7cm × 3cm × 0.5cm). The maximum duration time of the tests was 24 h at 30, 40, 50 °C in solutions. At the end of the tests, the specimens were carefully washed with bi-distilled water then degreased with acetone under ultrasound and then weighed. Triplicate experiments were performed in each case and the mean value of the weight

loss is reported. The concentrations of inhibitor employed in corrosion measurements were (1×10^{-5} , 5×10^{-5} , 1×10^{-4} , 5×10^{-4} , 1×10^{-3} , 5×10^{-3} and 1×10^{-2} M) at 30, 40 and 50 °C in 1 M HCl. All solutions were prepared from bi-distilled water.

3.7.2. Electrochemical measurements

Polarization measurements were carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell. All the experiments were done at 30 ± 0.1 °C in solutions open to the atmosphere under unstirred conditions for 30 min. of exposure time which was determined as described elsewhere. Working electrode (WE) in the form of rod from steel and is embedded in polytetrafluoroethylene (PTFE). The geometric area of the electrode exposed to the electrolyte was 0.7 cm^2 . A saturated calomel electrode (SCE) and a platinum electrode are used as reference and auxiliary electrodes, respectively as shown in Fig. (70). The polarization curves were recorded by using a Voltalab 40 Potentiostat PGZ 301. A Pentium IV computer with voltmaster 4 software processed data. The potential scan rate 10 mV/s. Potential was scanned in the potential range of -900 to -250 mV.

The aggressive solution (1M HCl) was prepared by diluting the appropriate concentration of an analytical reagent grade of hydrochloric acid (37 %) with bi-distilled water.

The concentrations of inhibitor employed for corrosion measurements were (1×10^{-5} , 5×10^{-5} , 1×10^{-4} , 5×10^{-4} , 1×10^{-3} , 5×10^{-3} and 1×10^{-2} M) at 30 °C in 1 M HCl. All solutions were prepared from bi-distilled water.

(a) Reference electrode

It was a saturated calomel electrode (SCE) was prepared by using pure chemicals. The calomel paste was shaken with repeated changes of saturated KCl before it was introduced in the container over the pure mercury. Over the surface of the calomel paste, there were always present crystals of KCl in

order to ensure saturation with that compound. This electrode was written as following:



(b) Auxiliary electrode

A platinum wire as an auxiliary electrode was made of the purest metal and was sealed into glass tube filled with mercury for electrical connection. Before using the electrode, it is cleaned by dipping into hot HCl solution, washed with running water, distilled water and finally rinsed with little amount of the electrolyte solution.

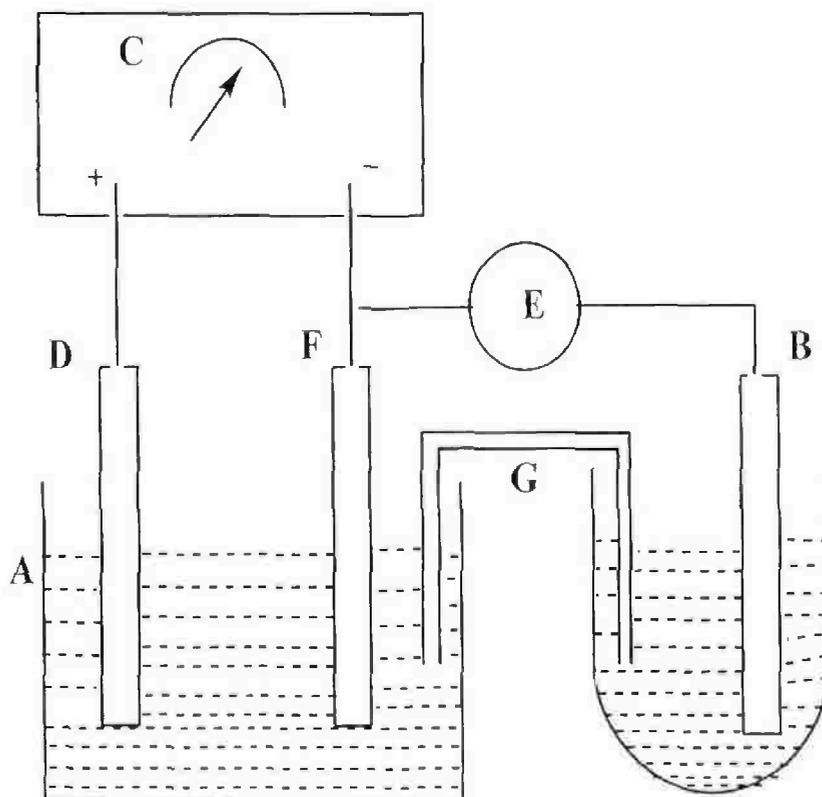


Fig. (70): The electrical circuit for cathodic polarization measurement.

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|--------------------------|---------------------|
| A: Polarization cell | E: Potentiometer |
| B: Reference electrode | F: Sample electrode |
| C: Constant current unit | G: Salt bridge |
| D: Auxiliary electrode | |

Experimental

(c) Working electrode

The working electrode has the chemical composition was given in **Table (24)**. The sample steel in the rod forms. The surface area exposed to corrosion is 1.05 cm^2 . The rode was weld from one side to a copper wire was used for electric connection. The sample was embedded in glass tube of just larger diameter than it was. The epoxy resin was used to stick the sample to glass tube as shown in **Fig. (71)**.

This also insured that constant cross-sectional area was grinded with different apperceive papers in the normal way, initially with course grade and gradually to biner ones, then finally with the finest grade polishing using alumina paste on mechanical polisher for finally polishing of sample surface to be mirror bright, followed by washing with distilled water then with acetone and finally with doubly distilled water, just before insertion in the electrolyte cell.

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Chemical composition of the carbon steel samples

The chemical composition of the carbon steel samples was determined using emission spectrometer, with the aid of ARL quantimeter (model 3100-292 IC). The chemical composition of steel sample was recorded in **Table (25)**.

Table (25): The chemical composition of carbon steel 52/3 (37) sample.

C	Si	Mn	P	S	Al	Fe
0.21	0.38	0.05	0.09	0.05	0.01	Rest

3.8. Scanning electron microscopy (SEM)

Immersion corrosion analysis of carbon steel samples in the acidic solutions with and without the optimal concentration of the inhibitor was performed using SEM. Immediately after the corrosion tests, the samples were subjected to SEM studies to know the surface conditions. SEM Jeol JSM-5400 was used for the experiments.

3.9. Antimicrobial activity

The antimicrobial activity of the synthesized products was measured against bacteria (SRB).

1-Source of microorganisms:

The tested organisms obtained from the unit of Micro Analytical Center, Cairo University, Cairo, Egypt.

2-The media

The following media was used in the antimicrobial activity of the synthesized products. The bacterial species grow on nutrient agar. Nutrient agar consists of 3 g/l beef extract, 5 g/l peptone, 3 g/l sodium chloride and 20 g/l agar. Then, complete the volume to one liter, heated the mixture until the boiling and sterilize the media by autoclave.

The tube dilution technique

1. Account the number of lived microorganism in blank solution.
2. In this procedure, the biocide in test tubes diluted out in the growth medium in a dilution series.
3. All the tubes then incubated with the organism in test tubes.