CHAPTER (3)

MATERIALS AND EXPREMENTAL TECHNIQUES

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3. MATERIALS & EXPERIMENTAL TECHNIQUES

3.1. Materials

Table (1):-The Chemicals used throughout the investigation in this work

Material	Purity	Molecular weight (gm)	Source
Sodium metal	Issued in liquid paraffin	23	B.D.H
Ethanol	99%	46.07	Adwic
Thiourea	98 %	76.1	Merck
1,6-dibromohexane	97%	243.98	Merck
1,8-dibromooctane	98%	272.03	Aldrich
1,10-dibromodecane	97%	300.09	Aldrich
1,12-dibromododecane	98%	328.14	Aldrich
Trisodium citrate	99%	258.07	Aldrich
Silver nitrate	99%	169.87	Merck
N-methylpyrrodilone	99%	99.13	Merck
Hydrochloric acid 37%	-	36.46	Panreac
3-Aminophenol	99%	109	Merck
sulfuric acid	98%	98	Adwic
Cerium(IV)-sulfate	99.7%	332.24	Alderich
Sodium hydroxide	99%	40.00	Adwic
Parrafine oil	-	-	Adwic

3.2. Synthesis

3.2.1. Synthesis of the monomeric thiol surfactants (C6M, C8M, C10M and C12M)

The monomeric surfactants were synthesized throughout two steps as follow.

3.2.1.1. Synthesis of 3-bromoalkyloxy aniline

3-bromohexyloxyaniline, 3-bromoctyloxyaniline, 3bromodecyloxyaniline and 3-bromododecyloxyaniline were prepared by reaction of (1:1) 3-aminophenol with 1,6-dibromohexane, 1,8-dibromoctane, 1,10-dibromodecane and 1,12- dibromododecane, respectively in presence of sodium ethoxide **[sayyah et al., 2006].**

3.2.1.2. Synthesis of 3-mercaptoalkyloxy anilines

The bromo group was converted into thiol via the isothiouronium salt by reaction with thiourea (1:1). 3-bromoalkyloxy aniline and thiourea were dissolved in ethanol (50 mL) and refluxed for 6 hours. The reaction mixture was concentrated and the residue was washed with hexane and crystallized from ethanol/hexane .this intermediate salt was dissolved in 50 mL of ethanol and then an aqueous solution (5 mL) of NaOH (70 mg) was added drop wise the mixture was refluxed for 3 hours. After neutralization with sulfuric acid the reaction mixture was concentrated. The residue was filtered off and washed with ethanol and then dried to obtain 6-(3-amino phenoxy) hexane-1- thiol (C6M), 8-(3-amino phenoxy) octane-1- thiol (C8M), 10-(3-amino phenoxy) decane-1-thiol (C10M), 12-(3-amino phenoxy) dodecane-1- thiol (C12M) respectively **[Tamada et al., 1998, Azzam et al., 2009, Ding, et al., 2008]**.

3.2.2. Synthesis of the polymeric thiol surfactants (C6P, C8P, C10P and C12P)

The chemical polymerization of 3-mercaptoalkyloxy aniline surfactants (C6M-C12M) was performed in presence of protonic acids. A solution of (3-mercaptoalkyloxy aniline and 0.5 M HCl) was added drop wise over a period 15 min into a vigorously stirred aqueous solution of $Ce(S04)_2$ kept at $80^{O}C$ After stirring for 8 hours., the precipitates produced were separated by filtration, washed firstly with 1 M HCl, then distilled water, methanol, and finally acetone, and then dried under reduced pressure at room temperature overnight to obtain poly 6-(3-amino phenoxy) hexane-1- thiol (C6P), poly 8-(3-amino phenoxy) octane-1- thiol (C8P), poly 10-(3-amino phenoxy) decane-1- thiol (C10P), poly 12-(3-amino phenoxy) dodecane-1- thiol (C12P) respectively **[Yan and Toshima, 1995]**.

3.2.3. Preparation of the Silver Nanoparticles

The silver nanoparticles colloidal solution was prepared by using chemical reduction method according to the description of Lee and Meisel **[Fang et al., 2005]** all solutions of reacting materials were prepared in distilled water. In typical experiment 50 mL of $1x10^3$mol/L $AgNO_3$ was heated to boiling. To this solution 5 mL of 1 % trisodium citrate was added drop by drop. During the process solution was mixed vigorously. Solution was heated until colour's change is evident (pale yellow). Then it was removed from the heating element and stirred until cooled to room temperature **[Sileikaite et al., 2006]**.

3.2.4.1. Preparation of the nanostructure of the monomeric thiol surfactant with the silver nanoparticles

The silver nanoparticles solution (20 mL) was mixed with 5 mL saturated solution of the synthesized monomeric thiol surfactants (C6M, C8M, C10M and C12M) in deionized water and stirred continuously for 24 hour till the yellow colour faded. The resulting solution was used for ultra violet experiments and TEM image then the resulting solution was centrifuged at 12000 rpm to obtain the precipitate of thiol-coated silver nanoparticles. The precipitate was washed with cold water to remove any unreacted. The washed precipitate was used for infrared experiments and XRD analysis.

3.2.4.2. Preparation of the nanostructure of the polymeric thiol surfactant with the silver nanoparticles

The silver nanoparticles solution (20 mL) was mixed with 5 mL saturated solution of polymeric thiol surfactants (C6P, C8P, C10P and stirred continuously for 24 hour till the yellow colour faded. The resulting solution was used for ultra violet experiments and TEM image then the resulting solution was centrifuged at 12000 rpm to obtain the precipitate of thiol-covered silver nanoparticles. The precipitate was washed with cold water to remove any unreacted. The washed precipitate was used for infrared experiments and XRD analysis.

3.3. Experimental Techniques

3.3.1. Fourier Transform Infrared Spectrometer (FTIR)

All 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). The FTIR were carried out in Egyptian Petroleum Research Institute.

3.3.2. Proton Nuclear Magnetic Resonance (^{1}HNMR)

^{1}HNMR measurements were performed on a Varian-Germini-200 instrument and the measurements were carried out at the National Research Centre.

3.3.3. Ultraviolet Absorption Measurements (UV)

The UV measurements were carried out by hp deskjet 920c scan UV photometer. The measurements were carried out in Egyptian Petroleum Research Institute.

3.3.4. X-Ray Diffraction Measurements (XRD)

X-ray diffraction patterns were recorded with a Pan Analytical Model X' Pert Pro, which was equipped with CuKα radiation ($\lambda = 0.1542$ nm), Ni-filter and general area detector. The diffractograms were recorded in the 2θ range of 0.5–10 with step size of 0.02 Å and a step time of 0.605. The measurements were carried out in Research Central Metallurgical Research and Development Institute.

3.3.5. Thermal Gravimetric analysis (TGA&DSC)

Wax thermal catalytic cracking were carried out in a TA Instruments SDTQ 600 simultaneous TGA-DSC thermogravimetric analyser. The samples were heated under nitrogen flow (100 ml min^{-1}) from 50 to 800 ^{O}C, at 20 ^{O}C min^{-1}. This step was carried out at, Egyptian Petroleum Research Institute

3.3.6. Surface and Interfacial Tension Measurements

Determination of surface and interfacial tension of the solution was carried out at 25 ^{O}C using Kruss Du Noüy tensiometer, Type K6 (Krüss GmbH, Hamburg, Germany) **[Azzam, et al., 2004]**. This step was carried out at Applied Surfactant Laboratory., Petrochemicals department, Egyptian Petroleum Research Institute.

3.3.7. Emulsion Stability

Samples were prepared by addition of 6 mL of paraffin oil to 10 mL of (0.1 mol/L) solution of the surfactant. After shaking for 15 sec, the mixture was allowed to set and the time for the two layers to separate was measured **[Azzam, et-al., 2004]**. The measurements were carried out at Applied Surfactants Laboratory., Petrochemicals Dept., Egyptian Petroleum Research Institute.

3.3.8. Transmission Electron Microscope (TEM)

A convenient way to produce good TEM samples is to use copper grids. A copper grid pre-covered with a very thin amorphous carbon film. To investigate the prepared AgNPs and the nanostructure of synthesized surfactants with AgNPs using TEM, small droplets of the liquid was placed on the carbon-coated grid. 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. The measurements were carried out at the National Research Centre.

3.3.9. Evaluation of the synthesized surfactants without and with AgNPs as Corrosion Inhibitors

The synthesized monomeric and polymeric surfactants and their nanostructure with the prepared AgNPs was Evaluated as Corrosion Inhibitors by three methods as following

3.3.9.1. Weight loss Technique

The carbon steel coupon of 7 cm 1.5 cm 0.5 cm was used. The chemical composition of steel sample was recorded in Table (2). The carbon steel coupons abraded with a series of emery paper (grade 320-500-1000-1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in 250 ml bottle, which contained 150 mL hydrochloric acid 1 molar with and without addition of different concentrations (75, 150, 225, 300, 375 ppm) of prepared compounds. After 10 hours, the specimens were taken out, washed, dried, and weighed accurately. The experiments were carried out in triplicate. The average weight loss of three parallel carbon steel coupons could be obtained. Then the tests were repeated at (25°C).

Table (2):- The chemical composition of steel sample

Element	Fe	C	Al	Si	P	S
(%)	98.798	0.26	0.637	0.255	0.031	0.019

3.3.9.2. Polarization Technique

Polarization experiments were carried out in potentiostat Volta Lap 40 PGZ 301 with conventional three electrodes, a platinum counter electrode, saturated calummel electrode and working electrode. Before measurement, the electrode was immersed in test solution at natural potential for one hour until a steady state was reached. The potential increased with scan rate of 1mVs^{-1} and started from potential of-800 to -350 mV. The measurements were carried out at Applied Surfactants Laboratory, Petrochemicals Department, and Egyptian Petroleum Research Institute.

3.3.9.3. Energy Dispersive Analysis of X-rays (EDAX)

EDAX system attached with a Joel 5400 scanning electron microscope was used for elemental analysis or chemical characterization of the film formed on steel surface. As a type of spectroscopy, it relies on the investigation of sample through interaction between electromagnetic radiation and the matter. So that a detector was used to convert X-rays energy into voltage signals. This information is sent to a pulse processor, which measure the signals. The measurements were carried out in Egyptian Petroleum Research Institute.