Experimental Part

CHAPTER II

EXPERIMENTAL

Chemicals Used

All used chemicals throughout this investigation are provided from international companies as shown in **Table 1**.

Table 1: Chemicals Used.

Materials	M.wt.	Purity %	m.p. °c	b.p. °c	Source
Triethanolamine	149.19	99	17.9	190-193	Aldrich, USA.
Sodium hydroxide	40	97	-	-	Aldrich, USA.
Oleic acid	282.4	Technical	13.4	194	Adwic, Egypt.
Ethylene oxide	44.05	99.5	-111	10.7	Merck, Germany.
Triethylamine	101.19	99	-115	88.8	Aldrich, USA.
Xylene	170	AR	12-13	138-140	Aldrich, USA.
Isopropanol	68.16	Technical	-	82	Bio.Chem, Egypt.
Hydrochloric acid	36	36.5	-	-	Adwic, Egypt.
Acetone	58	99	-94	56.5	Aldrich, USA.
Ethanol	46.07	Technical	-130	78`	Adwic, Egypt.
Acetic acid	60.05	99.8	16-16.5	116-118	Aldrich, USA.
Commercial inhibitor	-	-	-	-	SECA, Co.

Polymerization of Triethanolamine

Polytriethanolamine was prepared by condensation polymerization of triethanolamine (1 mol, 149 g) in the presence of 0.04 mol sodium hydroxide as a catalyst in a three-neck round-bottomed flask equipped with a refluxing condenser, a stirrer, and a thermometer. The

triethanolamine was heated at 245 °C for three different times 1.30, 2.30, and 3.30 hours under azeotropic separation condensation. Water was collected in a Dean-Stark apparatus. The products are abbreviated as P_x, whereas x noted to the degree of polymerization (4, 6, and 8). Then they were purified by washing with a solution of 5% acetic acid and then dissolved in petroleum ether (b.p. 40-60 °C). The petroleum ether layer was separated and the solvent was distilled under vaccum to give the pale yellow viscous liquid polymer [76].

Esterfication of Polymers With Oleic Acid

The prepared polymers were esterfied at different molar ratios with oleic acid (P : O ; 1 : 1 to 1 : 7) in a three-necked flask in the presence of p-toluene sulfonic acid (0.1 wt %) as a catalyst. The reaction mixture was heated at 150 °C with continuous stirring until the theoretical amount of water was collected. The product was purified by washing with a hot solution of supersaturated sodium chloride. The organic layer was separated and the solvent was distilled off to give esters.

Ethoxylation of Polymer

A high pressure stainless steel autoclave (Parr model 4530, USA) of 1L capacity, 400 psi maximum pressure and 450 °C maximum temperatures was utilized for ethoxylation reaction. The autoclave is equipped with a magnetic drive stirrer, an electric heating mantle with a thermocouple inserted in the reactor body, a cooling coil, a pressure gauge and a drain valve.

The prepared polymer (P_8) was charged into the reaction vessel with triethylamine as a catalyst (0.3 wt %) and the reaction mixture was heated to 80 °C with continuous stirring while passing a stream of nitrogen gas through the system for 10 minutes to flush out air [77]. The nitrogen stream was then replaced by ethylene oxide. Three different molar ratios of ethylene oxide namely (n= 40, 100 and 120 EO moles) were introduced to P_8 through the inlet gas valve until the desired amount of ethylene oxide was introduced. Generally, as a result of the introduction of ethylene oxide, the pressure was substantially increased as indicated by the pressure gauge, until it reached a maximum value. The pressure drop indicates ethylene oxide

consumption. The reaction completion was established when the pressure reached its minimum value. At this stage, heating was stopped and the contents were cooled gradually to ambient temperature by means of the cooling coil connected to the reactor carrying cold water. After cooling. the product obtained was discharged, weighed and neutralized with HCl, dissolved in isopropanol, then salted out with supersaturated NaCl solution. The organic layer was then separated and the isopropanol was distilled off [81,82]. The ethoxylated product obtained appeared as a brown viscous liquid appearance.

Esterification of the Ethoxylated Polymers

The ethoxylated polymers were esterified at different molar ratios with oleic acid in a three-necked flask in the presence of p-toluene sulfonic acid (0.1 gm %) as a catalyst and xylene as a solvent. The reaction mixture was heated at 140 °C with continuous stirring until the theoretical amount of water was collected. The product was purified by washing with a hot solution of supersaturated sodium chloride. The organic layer was separated and the solvent was distilled off.

The Chemical Structure of the Compounds Prepared was Confirmed by:

1. Elemental Analysis
2. FT-IR
3. ^{1}H, ^{13}C NMR (Massey University, New Zealand).

Evaluation of Some Surface Active Properties of the Compounds Prepared

Surface Tension Measurements (γ)

Surface tension measurements were obtained using De-Noüy Tensiometer (Kruss-K6 type) and applying a platinum ring technique. A freshly prepared aqueous solution of the synthesized polytriethanolamine derivatives in deionized water was prepared with a concentration range of 0.01-0.00001 M/L at 25 °C. The ring was washed twice after each reading

first by ethanol then distilled water. The apparent surface tension was measured 5 times for each sample within a 2 minute interval between each reading [78].

Critical Micelle Concentration (CMC)

CMC of the prepared surfactant was determined by the method adopted by Larinov [79]. 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) [80].

Surface Excess Concentration (Γ_{max})

Γ_{max} is a measure of the effectiveness of adsorption of surfactant at the liquid/air or liquid/liquid interface since it is the maximum value to which adsorption can be obtained [1].

Γ_{max} can be calculated from the Gibbs equation:

$$\Gamma_{max} = (1/RT)\,(\delta\gamma / \delta \ln C) \qquad (5)$$

Where:

Γ_{max} is the surface excess concentration (mol/cm^2),

T is the absolute temperature (273+°C),

R is the universal gas constant (R = 8.314 Jmol^{-1}deg^{-1}), and

$\delta\gamma / \delta$ **ln C** is the surface activity (slope of the linear portion of SVC curves) [81].

Minimum Surface Area per Molecule (A_{min})

A_{min} is the minimum area per molecule in nm^2/molecule at the interface [82]. The area occupied by each adsorbed molecule is given by equation:

$$A_{min.} = 10^{16} / (N_A . \Gamma_{max}) \qquad (6)$$

Where:

N_A is Avogadro's number = 6.023 x 10^{23} molecules/mol [83].

Effectiveness π_{CMC}

The surface tension (γ) values at CMC were used to calculated values of surface pressure (effectiveness) from the following equation [84,85].

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \qquad (7)$$

Where: γ_0 is the surface tension of water at 25 °C

γ_{CMC} is the surface tension value of the measured solution at CMC.

Thermodynamic Parameters of Micellization

The ability for micellization processes depends on the thermodynamic parameter (standard free energy, $\Delta G_{mic.}$). Most information on the free energy of micellization has been obtained indirectly through the CMC. [86]. The $\Delta G_{mic.}$ may be calculated by choosing the following expression equation (8), for the standard initial state of the non micellar surfactant species a hypothetical state at unit mole fraction X, with the individual ions or molecules behaving as at infinite dilution, and for the standard final state, the micelle itself.

$$\Delta G_{mic.} = 2.3\ RT\ (1-\alpha)\ \log CMC. \qquad (8)$$

Where:

R: the universal gas constant(R= 3.418 J/mol.K),

T: the absolute temperature (T= t+273), and

α: the fraction of counter ions bound by micelle in case of ionic surfactants (α=0 for nonionic surfactants), and

CMC: critical micelle concentration in g/mol.

Thermodynamic Parameters of Adsorption

Many investigations, deal with the thermodynamics of surfactant adsorption at the interface [87]. The thermodynamic parameters value of adsorption ΔG_{ads} were calculated via the following equation (9):

$$\Delta G_{ads.} = \Delta G_{mic} - 0.6023\ \Pi_{CMC}\ A_{min}.. \qquad (9)$$

Evaluation of the Compounds Prepared

1- As Corrosion Inhibitors.

Chemical Composition of the Investigated Carbon Steel Alloy

The chemical composition of the carbon steel used throughout this investigation is listed in **Table 2.**

Table 2: Chemical Composition of the Carbon Steel Used

Element	C	Mn	P	Si	S	Cr	Mo	Fe
Analysis (Weight %)	0.17	1.18	0.008	0.27	0.008	0.27	0.04	98.054

Test Specimens and Treatment

Weight Loss Measurements

The test specimens were used in the form of sheets of dimensions 7 x 2 x 0.2 cm, and average weight = 37.5 gm. These specimens were polished by 310, 410 and 610 emery papers, degreased with acetone, then washed with double distilled water and finally dried between two filter papers. Such treatment was carried out immediately before each measurement.

Solution Preparations

Hydrochloric Acid Solution

Approximately 5N hydrochloric acid solution was prepared by diluting the appropriate volume of the concentrated chemically pure grade acid with distilled water. The concentration of acid was checked by titration against standard solution of sodium hydroxide. From this stock concentrated solution, exactly 1N hydrochloric acid solution was prepared by dilution with distilled water.

The Inhibitor Solution

The corrosion inhibitor solutions were prepared by dissolving the desired weight of the surfactants in distilled water. Seven different concentrations (above and below the CMC) 50, 100, 200, 300,400,500 and 600 ppm were used throughout the corrosion inhibition evaluation.

Procedures Used for Corrosion Measurements

Weight Loss Measurements

The specimen of the given metal was prepared as described before (total surface area = 31.6 cm^2) and dipped in 150 ml of the test solution at different temperatures viz, 298, 308, 318, 328 and 338 K. The 1M HCl solution was used as a blank for weight loss measurements. This was carried out in covered beaker to prevent contact with air and minimize the escape of evolved gases. After the required immersion time, the test specimen was removed, washed with double distilled water, dried by a jet of air and finally weighed. The change in weight was recorded to the nearest 0.0001. Precautions were always made to avoid scratching of the specimen during washing after exposure.

The weight loss was calculated by the following equation:

$$\Delta W = W_1 - W_2 \qquad (10)$$

Where: W_1 and W_2 are the weight of specimens before and after reaction, respectively

and inhibition efficiency was determined by the following equation

$$\eta\ \% = \frac{\Delta W - \Delta Wi}{\Delta W} x100 \qquad (11)$$

Where, ΔW and ΔWi are the weight loss per unit area in absence and presence of inhibitor, respectively. Through studying the effect of inhibition efficiency, the rate of corrosion (C.R) was calculated by the following equation [88].

$$C.R = \frac{W \times 3.45 \times 10^6}{A \times t \times D} \qquad (12)$$

Where: W, is mass loss in grams, A, is area in cm^2, t, is the immersion time in hours, D, is density in g/cm^3.

As Emulsion Breakers [Demulsifiers]

Crude Oil Types

Asphaltenic crude oils were supplied by the GENERAL Petroleum Company ,Cairo, Egypt The general physicochemical properties of the crude oil type are shown in **Table 3.**

Table 3: Physicochemical Properties of the Crude Oils Used

Specification	Method	Asphaltenic crude-oil
Specific gravity (60/60° F)	IP160	0.973
API gravity at 60° F	IP160	36.29
Kinematic Viscosity at 40°C (C.St.)	IP 71	294.972
Asphaltene Content (wt.%)	IP 143	9.45%
Paraffin wax (wt.%)	UOP 46	2.86%
Water Content	IP 74/70	0.5%

Sea-Water

Physicochemical characterization of the sea water is shown in **Table 4.**

Table 4 : General Characters of Sea Water Sample

Total dissolved solids	44372	mg/L	**pH**	7.74	at 19 °C
Resisitivity	0.019	Ohm at 19 °C	**Salinity**	39996	mg/L
Conductivity	52.2	mS/M at 19 °C	**Sp. Density**	1.03304	
Density	1.032	g/ml			
Constituents	mg/L	meq /L	**Constituents**	mg/L	meq /L
Sodium	13431	584.2	**Hydroxide**	Nil	Nil
Calcium	478.3	23.86	**Carbonate $^{--}$**	Nil	Nil
Magnesium	1634	134.46	**Bicarbonate^{-}**	135	2.21
Potassium	488.6	12.49	**Chloride^{-}**	24240	683.8
Lithium	0.603	0.046	**Sulfate^{--}**	3329	69.31
Barium	0.1774	0.00026			
Strontium	8.86	0.20			
Iron	0.0084	-			
Aluminum	Nil	Nil			
Copper	Nil	Nil			

Water-in-Crude-Oil Emulsions

Naturally occurring crude oil emulsion (w/o) was supplied by the General Petroleum Company, Cairo, Egypt. The Bs & w was 50% (total base sediment and water).

Bottle Test

The bottle test was used to estimate the efficiency of demulsifiers to resolve the water-in-oil emulsions. Each demulsifier was dissolved in xylene added to (100ml) of the water-in-crude oil emulsion at different concentrations (in ppm). The mixture was added to a (100ml) graduated bottle test tube and then shaken for 1 min. The bottle was placed in a thermostated water bath at

60 °C. Water separation (in ml) was observed at different time intervals depending on the efficiency of the tested demulsifiers . A blank was used in each set of experiments [89].

The General Formulas of the Compounds Prepared

1- Polymer (P_n)

2- Ethoxylated ester of polymer $E(en)P_nO_m$

3- Ethoxylation of the polymer $E(en)P_n$

4- Ester of the polymer (P_nO_m)

Wherein,

n = degree of polymerization,

m = oleic acid polymer molar ratio

en = number of ethylene oxide units.