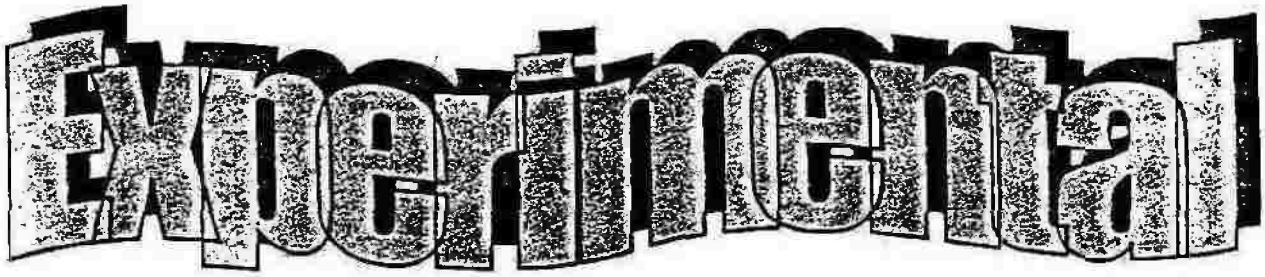

Experimental

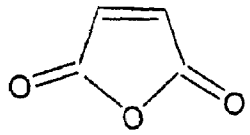
# 2. EXPERIMENTAL

## 2.1. RAW MATERIALS

### 2.1.1. Acids and Acid Anhydrides

#### *a- Maleic Anhydride (MA)*

Formula:



This dibasic acid was obtained from Aldrich Chemical Co. Ltd. (UK). It is a white flakes, having molecular weight 98.06 g/mol, melting point 54-56°C and boiling point 200°C.

#### *b- Acrylic Acid (AA)*

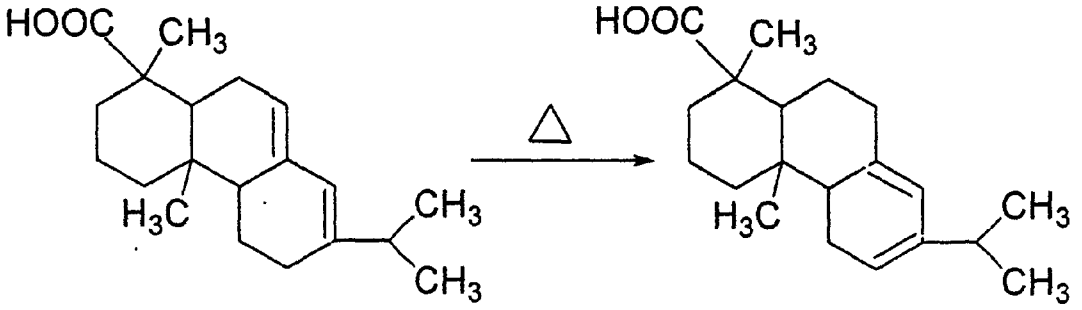
Formula:

$$H_2C=CH-COOH$$

It was obtained from Aldrich Chemical Co. Ltd. (UK) with the following specifications: molecular mass 72.06 g/mol, boiling point 139°C and density 1.051g/cm$^3$.

*c- Rosin Acids*

Rosin is a solid resinous material obtained naturally from pine trees. Rosin is composed of approximately 90 % rosin acids (abietic and pimaric acids) and 10 % non acidic materials. Rosin was heated at 150°C for 4 hr then heated at 200°C for 0.5 hr in nitrogen atmosphere to isomerize to leveopimaric acid, then it was separated by crystallization from the cold acetone solution of commercial rosin.




Abietic acid Levopimaric acid

*d- Stearic Acid (ST)*

Formula:

$$C_{17}H_{35}COOH$$

It was purchased from Aldrich Chemical Co. Ltd. (UK) with the following specifications:

<M.wt> : 284.4 (g/mol)

MP : 67-69 °C , BP : 183-184 °C.

*f- ρ-formaldehyde*

formula:

$$HO\text{-}(CH_2O)_n\text{-}H \quad (n \text{ equals } 8 \text{ to } 100)$$

It is a white solid powder obtained from Aldrich Chemical Co. Ltd. (UK) with melting range 120-170°C.

## 2.1.2.Polyethylene Glycols

General formula:

$$H(OCH_2\ CH_2)_nOH$$

They were purchased from Aldrich Chemical Co. Ltd. (UK) as ultra pure compounds, they are:

### *a) Polyethylene glycol 600 (PEG600)*

It is highly miscible with water and it has the following specifications:

<M.wt> : 600 g/mol

Viscosity (98°C) : 7.3 C.St

Softening temperature: -6 °C

### *b) Polyethylene glycol 1000 (PEG1000)*

It is hygroscopic waxy solid, soluble in water with the following specifications:

<M.wt.> : 1000 g/mol

Viscosity (98°C) : 17.4 C.St, Melting range: 33-40°C

*c) Polyethylene glycol 2000 (PEG2000)*

It is white water soluble flakes with the following specifications:

<M.wt.>: 2000 g/mol

Melting range: 50-53 °C

## 2.1.3.Catalyst and Inhibitor

*a)ρ-Toluene sulphonic acid*

$(CH_3C_6H_4SO_2)_2O$

<M.wt.>: 190.22

M.P. :124-126 °C

*b) Inhibitor (Hydroquinone) (HQ)*

It is a white solid crystal obtained from Aldrich Chemical Co. Ltd. (UK) with the molecular mass 326.44 g/mol., melting point 173-175°C. HQ was used as an inhibitor to stop the polymerization of acrylic and maleic anhydride monomers.

## 2.1.4 . Solvents

High purity grade toluene, ethanol, acetone, pyridine, acetic Acid & its anhydride, and methylene chloride were purchased from Aldrich as analytical reagents and used as received.

| Solvent | Source | b.p(°C ) |
|---|---|---|
| Acetone | Aldrich Chemical Co.Ltd (USA) | 56 |
| Tolune | Aldrich Chemical Co. Ltd (USA) | 111 |
| Xylene | Aldrich Chemical Co. Ltd (USA) | 138 |
| Methanol | Aldrich Chemical Co.Ltd (USA) | 64 |
| Benzene | Aldrich Chemical Co. Ltd (USA) | 80-81 |
| Chloroform | Aldrich Chemical Co. Ltd (USA) | 60-61 |

### 2.1.5. Petroleum Crude Oil

Two types of crudes were used throughout this work:

- Baker crude oil (asphaltenic crude oil) was submitted from General Petroleum Co., Egypt. Its general specifications are listed in Table (2.1).
- The Qarun base crude oil (waxy crude oil) was submitted from Qarun Petroleum Co., Egypt. Its general specifications are listed in ***Table (2.2).***

### 2.1.6. Sea-Water

The sample of sea–water was collected from the Mediterranean Sea, Alexandria, Egypt. Its physicochemical characterizations are shown in ***Table (2.3).***

*Table (2.1): Specifications of Baker Crude Oil*

| Test | Method | Value |
|---|---|---|
| *API gravity at 60 F* | ASTMD-1298 | 21.7 |
| *Viscosity at 60 F (Cst)* | IP71 | 762.8 |
| *Specific gravity at 60 F* | ASTM D-1298 | 0.843 |
| *Asphaltene Contents (WT%)* | IP 143/84 | 7.83 |

*Table (2.2): Specifications of of Qarun Crude Oil*

| *Test* | *Method* | *Value* |
|---|---|---|
| *API gravity at 60 F* | ASTMD-1298 | 41.1 |
| *Specific gravity at 60 F* | ASTM D-1298 | 0.820 |
| *Wax content,(Wt%)* | UOP 46/64 | 16 |
| *Asphaltene content, (Wt%)* | IP 143/84 | 3 |

## *Table (2.3) : General characterization of Seawater*

| **Total dissolved solids** | 44372 Mg/l | | ***PH*** | 7.74 at 19,$^0$C | |
|---|---|---|---|---|---|
| **Resistivity** | 0.0191 Ohm m at 19 $^0$C | | ***Salinity*** | 39996 | Mg/l |
| **Conductivity** | 52.2 mS.M at 19, $^0$C | | ***Sp. Density*** | 1.03304 | |
| **Density** | 1.0322022 g/ml | | | | |
| **Constituents** | mg/l | Meq/l | ***Constituent*** | 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*** | 3329.02 | 69.31 |
| **Barium** | 0.1774 | 0.00026 | | | |
| **Strontium** | 8.86 | 0.20 | | | |
| **Iron** | 0.0084 | | | | |

## 2.2. PROCEDURES

### 2.2.1. Synthesis of the Rosin Diels – Alder Adducts

**a)** ***Synthesis of maleopimaric acid MPA***

Maleopimaric acid (MPA) was synthesized according to the following method: 90g (0.298 mol) of levopimaric acid and 29.5 g (0.3 mol) of MA were melted and reacted at 150°C for 2 hr under $N_2$. The cooled solid mass was dissolved in diethyl ether and slowly poured into hexane to give crude MPA (m.p:220°C), washed with ice-cold glacial acetic acid and dried under vacuum at 130-140°C for 5 hr (m.p: 229°C, yield 57%).

***b) Synthesis of acrylopimaric acid (APA)***

In 1L flat bottom flask, 10g rosin and 2.4g acrylic acid containing 0.5% hydroquinone were heated under $N_2$ at 140°C for 2 hr, 160 °C for 2 hr and finally at 175°C for 1 hr. The solid mass was then cooled and washed thoroughly and repeatedly with water to remove unreacted acrylic acid. The adduct was finally purified by reprecipitation with petroleum ether from diethyl ether solution.

### 2.2.2. Synthesis of MPA-PEG and APA-PEG ester

A mixture of freshly distilled PEG (1 mole), MPA or APA (1 mole), PTSA (1%) based on total weight of reactants and 20 ml xylene were placed in 0.5 L round-flask fitted with Dean Stark apparatus ***Figure (2.1).*** The mixture was allowed to reflux until (4ml) of water was collected. Xylene was distilled off from the reaction product by rotary evaporator under reduced pressure.

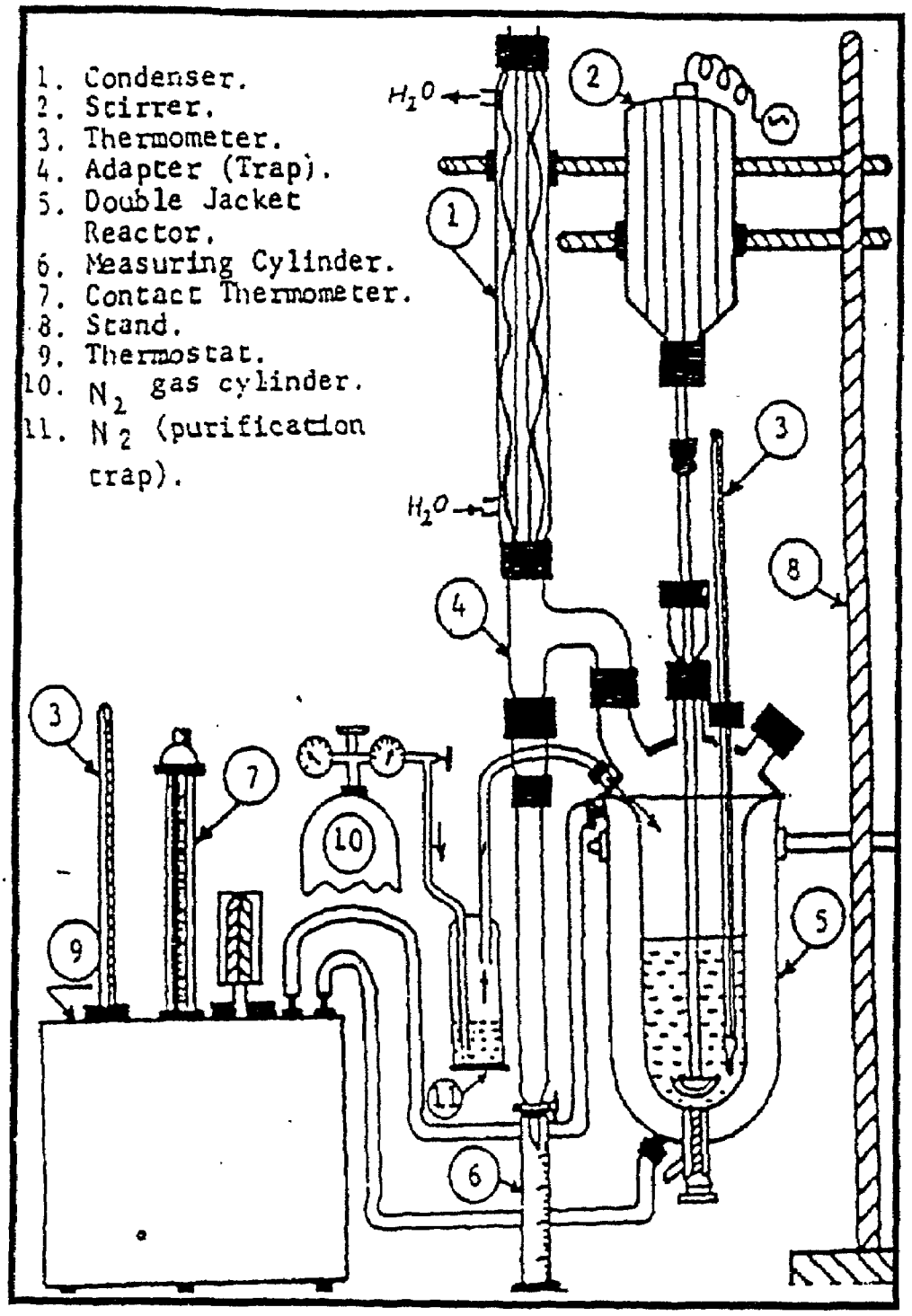



*Figure (2.1): Esterification Reaction Flask*

### 2.2.3. Synthesis of rosin acid-p-formaldehyde

A four necked flask fitted with a condenser was charged with 0.1mol of rosin acid and 100 ml toluene. The mixture was heated with stirring, under a slow $N_2$ stream and 0.1 mol of paraformaldehyde (FA) was added. The reactions were carried out in a resin kettle ***Figure (2.1)*** in the presence of p-toluene sulphonic acid (PTSA) as catalyst. PTSA (1% based on the weight of reactants) was introduced at 60°C. After a short time a vigorous exothermic effect was observed and the temperature rose up to 97°C. The methylolization of rosin acid was performed at 97°C for 90 min. Then a Dean-stark separator was fitted to the flask (Figure 2.1) and the reaction mixture was refluxed over a period of 60 min. As a consequence of gradual removal of the water, the boiling temperature rose continuously up to 130°C. The condensation reaction was continued with rise temperature up to 150°C and maintaining at this level for a period of 180 min. This was achieved by extraction of the separated aqueous layer and of a small quantity of toluene. Both the solvent and unreacted FA were removed by $N_2$ bubbling. The obtained resins were dissolved in acetone, filtered and dried at 70°C under vacuum.

### 2.2.4. Condensation of rosin with FA at High Temperature

After a condensation of rosin with FA, as described in the previous method of condensation, at 150°C for 120 min, small quantities of water and toluene were gradually removed. As a consequence, the reaction temperature increased continuously up to 240°C during a period of 75-80 min. It was observed that the rate of water release increased at temperature higher than 180°C. The temperature of 240°C was maintained for 2h to definitely end of gas bubbles and water removed, during the course of reaction. The obtained resin was cooled, dissolved in acetone or chloroform filtered and dried at 70°C under vacuum. The solid resin was suspensed in hot cyclohexane (75°C, 1:5 weight ratios).

All the prepared compounds and their notations are supplied in ***table (2.4).***

*Table(2.4): The prepared compounds and their notations*

| *The compound* | *Notation* |
|---|---|
| *Acrylic acid adduct + PEG600* | *APA-PEG600* |
| *Acrylic acid adduct + PEG1000* | *APA-PEG1000* |
| *Acrylic acid adduct + PEG2000* | *APA-PEG2000* |
| *Maleic acid adduct + PEG600* | *MPA-PEG600* |
| *Maleic acid adduct + PEG1000* | *MPA-PEG1000* |
| *Maleic acid adduct + PEG2000* | *MPA-PEG2000* |
| *Rosin acid+paraformaldehyde+PEG600* | *RFA-PEG600* |
| *Rosin acid+paraformaldehyde+PEG1000* | *RFA-PEG1000* |
| *Rosin acid+paraformaldehyde+PEG2000* | *RFA-PEG2000* |
| *Rosin acid+paraformaldehyde+PEG1000+ST* | *RFA-PEG1000-ST* |
| *Rosin acid+paraformaldehyde+PEG2000+ST* | *RFA-PEG2000-ST* |
| *Poly(Rosin acid+paraformaldehyde+PEG2000)* | *RFAP-PEG2000* |
| *Poly(Rosin acid+paraformaldehyde+PEG2000+ST)* | *RFAP-PEG2000-ST* |

## 2.3. CHARACTERIZATION OF THE OBTAINED PRODUCTS

### 2.3.1. $^1$HNMR-Spectroscopy

The prepared compounds were dissolved in $CDCl_3$ and analyzed using Varian $^1$HNMR spectrometer model JNM-EX (300 MHz) for determining their chemical structures.

### *2.3.2.* IR-Spectroscopy

The chemical structures of the prepared compounds were characterized by FTIR-spectroscopy using FTIR-spectrophotometer type [Mattson-Infinity series bench to P 961]. The wave number and intensities of IR bands of the different types of the function groups were determined a between of 500-4000 $cm^{-1}$.

### 2.3.3. Gel Permeation Chromatography (GPC)

The molecular weights of the polymeric surfactants were measured by GPC Water model 600 E. The measurements were recorded at 303 K, mobile phase toluene HPLC grade, Styragel column and injection volume chart.

### 2.3.4. Determination of Hydroxyl and Acid Number

The hydroxyl value is determined by acetic anhydride/pyridine method as following: 2.0g of surfactant was weighed to the nearest milligram into a 100 ml round-bottom flask. To dissolve the sample, a mixture of 5 ml acetic anhydride and 25 ml pyridine was added by pipette. The solution is refluxed for 1h. The condenser was then washed out by the addition of 5 ml water through the top; the mixture was then heated for 5 min. The condenser tube and tip were washed with 25 ml methanol. When the mixture has cooled to room temperature, it was titrated with approximately 0.5N standard potassium hydroxide solution to phenolphthalein end-point. This is value "a", taken as mg KOH/g. a blank is then run on a mixture of the same volumes used above of acetic anhydride-pyridine reagent and water, this value is "b'.

$$OH_{no.} = \frac{0.5N \times 56.1 \times (a-b)}{Wt\ of\ sample} \qquad (2.1)$$

The acid value was determined by titrating the solution of the weighed quantity of resin in acetone, with a standard alcoholic KOH solution ($\simeq$ 0.5N) using phenolphthalein as an indicator.

$$COOH_{no.} = \frac{0.5Nx56.1x(a-b)}{Wt\ of\ sample} \qquad (2.2)$$

### 2.3.5. Surface Tension Measurements

Water-soluble polymers were subjected to surface tension measurements. Different concentrations of each sample were prepared and the surface tension at 293, 303, 313 and 323K was measured using a platinum plate tensiometer, model Kruss K9. A specially designed double jacket glass cell connected with a thermostated oil bath was used for maintaining the adjusted temperature. Doubly distilled water ($\gamma$ = 72 dyne/cm) was used for preparing the concentrated stock solutions of the grafts. Several concentrations were prepared by diluting the stock solution with doubly distilled water to the appropriate concentration to be used in the determination of critical micelle concentration (CMC). The diluted solutions were allowed to stand for 24 hr before the surface tension measurements were performed.

### *2.3.6.* Interfacial Tension

Spinning drop interfacial tensiometer, Model Kruss Site-04, was used for measuring the interfacial tension between

surfactants' aqueous solutions and crude oil as an oil phase for which the elongation of the injected drop in the capillary was measured at an adjusted temperature (298 K) and speed of rotation. The interfacial tension ($\gamma$) was calculated from the ***equation (2.3).***

$$\gamma = 3.427 \times 10^{-7} (0.17\ \delta)^3 \times n^2 \times \Delta\rho \qquad (2.3)$$

Where $\delta$, n and $\Delta\rho$ are the diameter of the drop, the speed of rotation and the density difference between the oil phase and the surfactant aqueous solution, respectively.

### *2.3.7.* Cloud Point

Different solutions of the prepared surfactants having 2 wt % of the polymer in both double distilled water and saline solutions (1-5 wt % NaCl) were prepared. Each solution was heated with stirring until it becomes turbid. Upon cooling, the turbidity starts to disappear. The temperature at which the solution becomes completely clear was recorded as the cloud point of this particular solution.

## 2.4. EVALUATION OF PREPARED SURFACTANTS AS OIL SPILL DISPERSANTS

### 2.4.1. The Screen Test Procedure [Qualitative method]

A quick comparative test method using small vials (25ml) was developed from the beaker test proposed by **[Fingas et al. (1992)]**. and was used for visual determination of the dispersant effectiveness. The crude oil sample (100µl) was carefully added to the surface of sea water (20 ml) and then a 1 cm deep vortex was created by slow magnetic stirring. The dispersant mixture (5µl) was added to the center of the vortex and the stirring rate was immediately increased and maintained at a maximum rate of 200 rpm over 60s period and then stopped.

The level of oil dispersion in the water was visually estimated after one min rest. The classification, A, was attributed to the resulting brown-black mixture when all the oil was dispersed in the water leaving on slick at the surface. Where the classification, E, was used to describe a total lack of dispersion, i.e all the oil was returned to the surface few seconds after the end of the stirring leaving the aqueous phase nearly transparent. The designation letters B-D represents intermediate situations. All screen tests were performed at ambient temperature.

## 2.4.2. Determination of efficiency index of oil spill dispersants [Fingas et al. (1990)] Warren Spring Laboratory Quantitative Test Method]

***Procedure***: 250 $cm^3$ of sea water (about 10 ± 0.5°C )was added to 1L separating funnel. This temperature should be maintained throughout the test by conducting the work in a suitably temperature controlled chamber. The separating funnel was kept in the rotatable rack and left unstoppered. About 5$cm^3$ of the test oil was transferred by a syringe to water surface. The syringe was weighed before and after use to calculate the weight of 5.0$cm^3$ of the oil. The oil was allowed to transfer to rest on the surface of the water for one minute. When the time on the stopwatch shows 2.5min from the addition of the oil, the rotation of the separating funnel was started and continue at 33±1rev /min for a further 2 min. The separating funnel was placed in the upright vertical position and allow the contents to stand undisturbed for exactly 1 min before running off 50 $cm^3$ of the oily water through the tap and collecting it in a 50$cm^3$ measuring cylinder. The time taken for this operation should not exceed 10s. The oily water was transferred from the measuring cylinder to the 100 $cm^3$ separating funnel and the measuring cylinder was washed twice with 10 $cm^3$

of chloroform and the washings were added to the separating funnel. The funnel was stoppered and shaked for 1 min. The phases were allowed to separate completely and run off the chloroform layer through a no.1 Whatman filter paper containing anhydrous sodium sulphate. The chloroform extraction was repeated twice more using 20 $cm^3$of chloroform on each occasion wash the filter with 20 $cm^3$ of chloroform and combine the dried extracts and washings in 100$cm^3$ volumetric flasks. Make up to the mark, stopper and mix well. Measure the absorbance of chloroform extract against a chloroform blank at 580 nm in glass of 5mm path length. Using the calibration graph then calculate the weight of oil contained in the 50 $cm^3$ oily water sample. Repeat the measurements to obtain three separate determinations on each of the two reference fuel oils.

The Efficiency Index, EI, is calculated from the following ***equation (2.4):***

$$\%EI = \frac{\text{Weight of oil in } 50cm^3 \text{ sample of oily water}}{\text{Total weight of oil added to separating funnel}} \times 100$$