Results and Discussion

3. RESULTS AND DISCUSSION

The high price of crude oil has led to research and development activities worldwide for the use of alternative, preferably renewable, resource materials as feedstock for polymers and petrochemicals. In an attempt to find a suitable alternative and renewable substitute for petroleum-based chemicals we have recently developed natural product based materials. The most important point to be noted here is that the supply of rosin will be unhindered as this is derived from a forest product abundantly available in India and many other countries. The principal components of rosin are rosin acids. These acids are monocarboxylic acids of alkyl hydrophenantherene.

Generally, the rosin acids can be divided into two subgroups: the pimaric- type acid, characterized by both methyl and vinyl substituents, and the abietic-type acid, bearing only a single isopropyl group at vinyl substitution. Gum rosin, which contains approximately 90 % of abietic acid and its isomers, is obtained from the exudation of pine trees. This natural product is used largely in the manufacture of paints and varnishes due to its low cost, fast drying properties, excellent solubility and compatibility with other rosins and oils and also due to ready availability **[Enos (1977)]**. Therefore, rosin is treated in a number of ways according to its applications. The most important types of chemically upgraded rosin are limed rosin, ester gum and maleic modified rosin.

Modified phenolic resins and a variety of treated rosins can be obtained by different methods such as hydrogenation, polymerization and disproportionation **[Enos et al. (1968) and Stonecipher et al. (1968)]**. Gum rosin was made to react with maleic anhydride to form the Diels-Alder adduct. The Diels-Alder adduct, MPA, is also known as maleopimaric acid. The molecule of MPA contains one carboxyl group and one anhydride group. The two reactive functionalities are capable of undergoing various chemical reactions with appropriate reagents.

The hydrophenanthrene ring system present in the rosin moiety of MPA offers thermal and oxidative stability to the MPA molecule. It is expected from the above structural similarities that MPA may be a suitable substitute for petrochemicals in most, if not all, of its applications. Since rosin is a cheap and renewable material, the price of MPA and its derivatives is expected to be lower than that of any petrochemical. The rosin applications can be increased by increasing its functionality. In this respect, the present work pertains to introduce some advanced compositions, based on rosin, to be used in synthesis of new dispersants.

Accordingly, the work is divided into six main sections that are:

1. Synthesis of nonionic surfactants based on rosin adducts esters which are produced from reaction of MPA with PEG having different molecular weights (600, 1000 and 2000 g/mol).
2. Synthesis of nonionic surfactants based on rosin acrylic acid adduct, APA, esters which produced from reaction of APA with PEG having different molecular weights 600, 1000 and 2000 g/mol.
3. Modification of rosin with formaldehyde to introduce methyloyl group to rosin acids which can react with stearic acid and esterification of PEG having different molecular weights (600, 1000 and 2000 g/mol) to produce new nonionic polymeric surfactants.
4. Measuring the surface activity of the prepared surfactants,

5. Evaluation of the prepared surfactants as oil spill dispersants and,
6. Investigating the structure- performance relationship for the prepared surfactants.

3.1. PREPARATION OF NONIONIC SURFACTANTS FROM ROSIN

Water-soluble synthetic polymers are a family of materials that have been developed commercially and studied scientifically at an accelerating pace in recent years. Many water soluble polymers because of their amphipathic structure and surface activity- are used as surface active agents. In previous work, nonionic oil soluble surfactants were prepared from rosin acid and used as flow improver of crude oil [**Al-Sabagh et al. (2002) and Atta et al. (2004) & (2005)**]. The present work deals with synthesis of water soluble nonionic surfactants from rosin acid adducts and from rosin and hydroxyl derivatives of rosin acids followed by esterification with different molecular weights of PEG.

3.1.1. Nonionic surfactants from rosin adduct

The first part of the present work aimed to produce nonionic polymeric surfactants from rosin acid adducts through formation of Diels-Alder adducts followed by esterification with PEG. In this respect, rosin maleic anhydride and rosin acrylic acid adducts were prepared via Diels- Alder mechanism. The Diels-Alder adduct of rosin and maleic anhydride, for example, has been extensively used as a raw material for polymers such as polyester imides, polyamide imides, etc. **[Zachary et al. (1965), Arimoto and Zinkel (1982), Holmbom et al. (1996), Harrison et al. (2000), Lee et al. (1995), Browers (1982), Savil & Okay (2001), and Xu et al. (2002)].**

In the synthesis of the rosin maleic anhydride Diels-Alder adduct, MPA, rosin in its levopimaric acid form acts as the diene and maleic anhydride acts as the dienophile. Similarly, acrylic acid, acrylonitrile, acrylate and methacrylate may act as the dienophile with rosin. Polymer synthesis from rosin acrylic acid was the point of concern of many authors **[Conix (1958), Larez et al. (1990) and Schulze et al. (1997)].** A mixture of rosin and acrylic acid along with some other alcohols were reacted together to obtain some polymeric compounds that used as emulsifiers **[Billmeyer (1971) and Schulze et al. (1997)].**

Furthermore, Penezek and Matvnia **[Penczcek and Matvnia (1974)]** reported the use of rosin acrylic acid adduct (APA) in preparation of unsaturated polyester (UP) derivatives. This adduct was used for the production of alkyd resins or as a paper sizing agent [**Conix (1958) and Larez et al. (1990)**]. Diels-Alder addition reaction, involving the double bonds of rosin acid, as diene with unsaturated carboxylic substances as dienophiles and transformation into organic poly basic acids was also achieved [**Atta et al. (2003)**]. Synthesis of maleopimaric acid (MPA) and acrylopimaric acid (APA) from rosin acids was also reported [**Atta et al. (2006)**].

The present work describes the esterification of PEG with MPA or APA to produce nonionic surfactants having different hydrophile-lipophile balance (HLB) and to study the effect of surfactant structure on its properties. In this respect, the APA was subjected to react with PEG having different molecular weights varied from 600 to 2000 at 180°C. The same reaction conditions were applied to obtain esters with MPA adducts. The obtained esters of MPA or APA with PEG600, PEG 1000 and PEG 2000 were designated as previously mentioned in the experimental section. The produced surfactants are soluble in water, toluene, xylene and $CHCl_3$.

Beside that, products with high ester yield can be obtained either by using catalysts or by adding one of the reacting components in large excess or even by removal of water. In view of this, the reaction took place at relatively high temperature in order to remove any water from the reaction medium to shift the reaction to complete esterification. Addition of PTSA significantly increased the reaction rate. The scheme of reaction with levopimaric as model component is given in ***Figure (3.1)***. The physicochemical properties of rosin and its derivatives are mentioned in ***Table (3.1)***.

The properties listed in ***Table (3.1)*** reveal that the color of the derivatives changes from yellow to reddish brown with replacing PEG 600 by PEG 2000. The PEG content in the reaction mixture was determined from acid number measurements. The pH of 1% of derivative was measured in water and listed in ***Table (3.1)***. The data indicated that pH became neutral as molecular weight increased from 600 to 1000 g/mol and decreased as molecular weight of PEG is 2000 g/mol. The conversion of carboxylic acid group into ester might be the reason for this change. This observation indicated complete esterification of carboxylic acid groups of MPA and APA with PEG600 and PEG1000. The hydroxyl and acid numbers (mg KOH/g), listed in ***Table (3.1),*** indicate that MPA-PEG600, MPA-PEG1000, APA-PEG600 and APA-PEG1000 were completely esterified with PEG which can be referred to reduction of the acid number values. In this respect, rosin acids were converted into esters and the ester yield exhibited reciprocal relationship with the acid number. Furthermore, the average molecular weights of the prepared rosin adduct esters were determined by GPC technique as provided in ***Table (3.1).*** The values of molecular weights indicated that the carboxylic groups of MPA and APA were completely esterified with PEG 600 and PEG1000.

On the other hand, polydispersity values derived from GPC measurement of all derivatives are near to one which indicated uniformity of the reaction products. The reason for complete esterification of MPA and APA with PEG600 and PEG1000 can be referred to complete compatibility between the reactants. This may be explained according to the solubility point of view. When PEG600 and PEG 1000 reacted with adducts can produced completely soluble products which increase the possibility to effective collision between the monoester and PEG to produce di and triester for APA and MPA, respectively. While PEG2000 can be reacted with APA and MPA to produce monoester adduct. This may be due to the coiling of MPA-PEG2000 and APA-PEG2000 monoester which decreases the possibility to produce di and triesters.

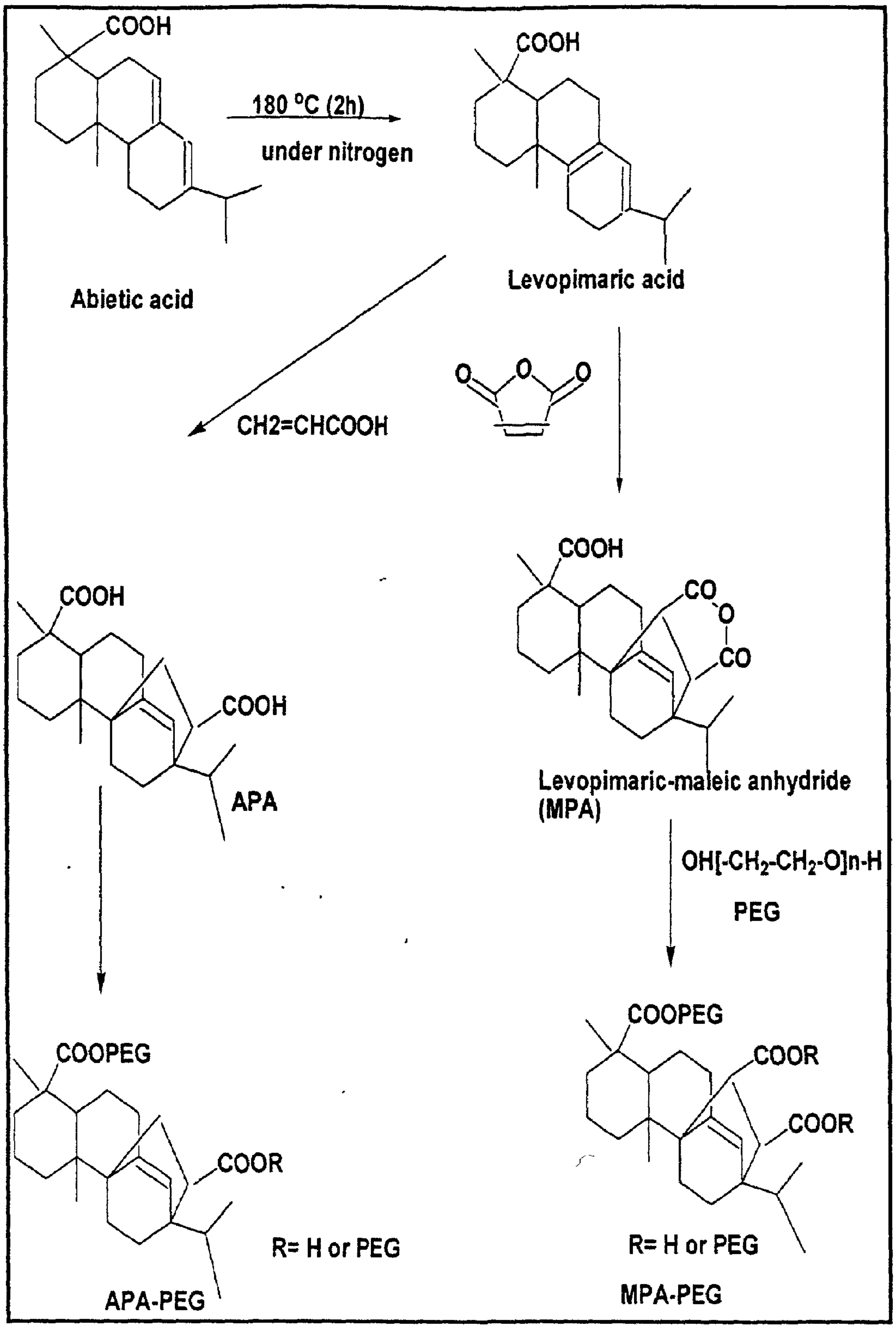


Figure (3.1): Scheme of Synthesis of MPA-PEG and APA-PEG Esters

Table (3.1): Physico-Chemical Properties of Rosin and Rosin Adduct Surfactants

Properties	Rosin	MPA-PEG600	MPA-PEG1000	MPA-PEG2000	APA-PEG600	APA-PEG1000	APA-PEG2000
Color & appearance	Pale yellow solid	Yellow solid	Brown solid	Reddish brown solid	Yellow Waxy solid	Brown Waxy solid	yellowish brown solid
Melting Point (°C)	167	45	50	55	38	45	51
Molecular weight[a]	303	2146	3346	4364	1511	2311	2329
Acid number[b]	183	3	5	47	2	2	25
Hydroxyl number[b]	0	46	28	12	72	46	23.17
pH of 1% suspension	5.81	6.12	6.5	6.02	6.8	6.89	6.05

[a] *Molecular weights were determined by GPC.*

[b] *Acid and hydroxyl number were measured as (mg KOH/g)*

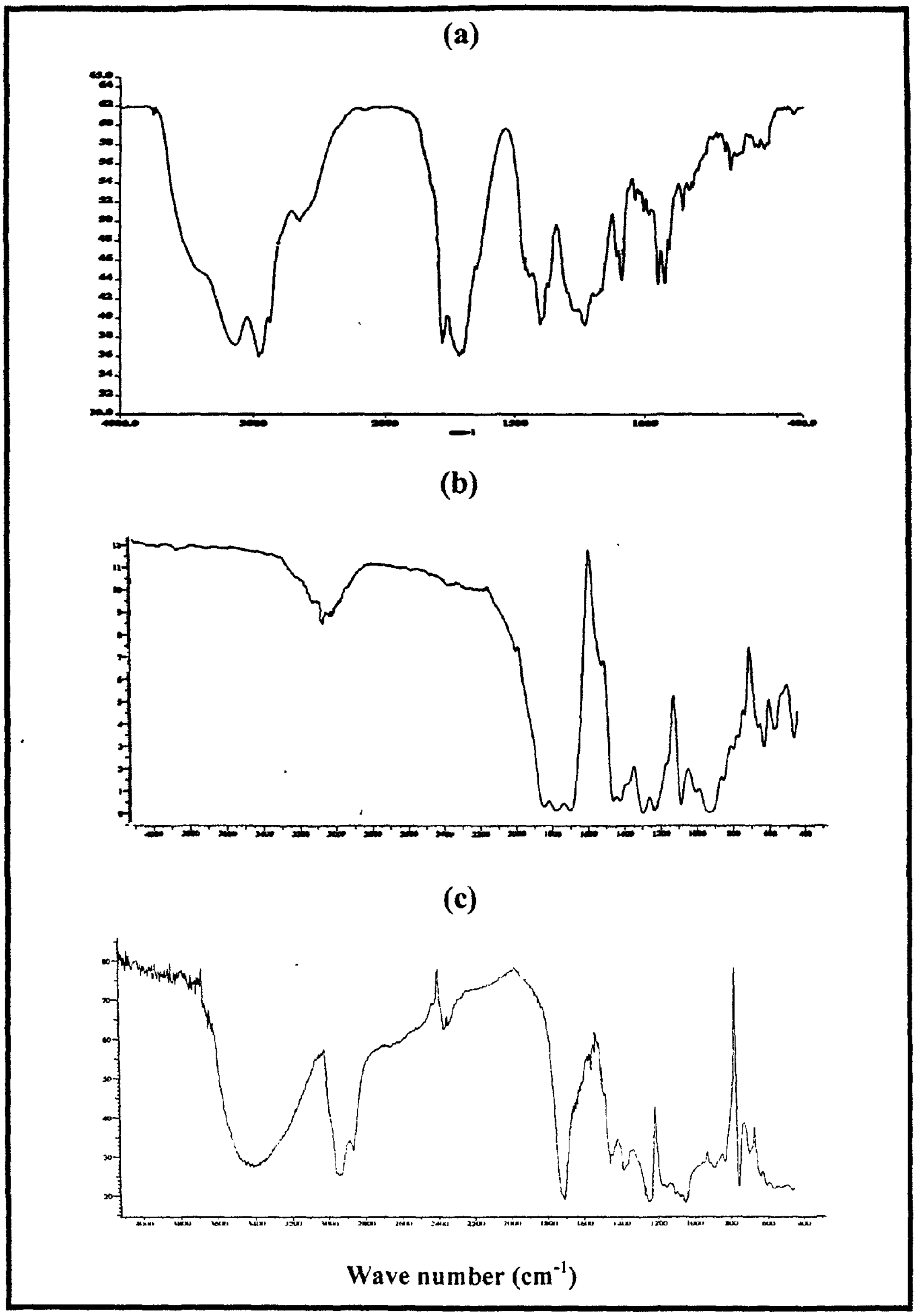
Moreover, the chemical structures of APA, MPA, APA-PEG and MPA-PEG were confirmed by IR spectroscopy. The IR spectra of APA and MPA compounds were represented in ***Figure 3.2 (a&b)***. It was observed that the spectra of all the esterified derivatives are nearly identical so the IR spectrum of MPA-PEG 600 was selected as representative sample and it is shown in ***Figure (3.2- c***). Careful inspection to the spectra in ***Figure (3.2 a&b)***, the following bands can be observed:

- The stretching band at 3450 cm^{-1} for OH.
- The characteristic band for γ C= O in COOH group at 1700 cm^{-1}.
- The double bond in hydrophenanthrene moiety at 1470 cm^{-1}
- $\gamma_{C=O}$ of cyclic anhydride group at 1780 & 1810 cm^{-1}.

The IR spectrum of MPA-PEG 600 ***Figure (3.2-c)*** shows the following characteristic bands:

- C=O stretching band at 1730 cm^{-1}.
- C-O of ether at 1110 cm^{-1}.

The esterification reaction of MPA with PEG can be confirmed by the disappearance of the bands characteristic to the cyclic anhydride group of in spectrum of MPA-PEG600 and the appearance of the ester band at 1730 cm $^{-1}$ ($\gamma_{C=0}$ sym in ester). The same bands were observed in all MPA-PEG and APA-PEG surfactants except MPA-PEG2000 and APA-PEG2000. There is one band observed in spectra of MPA-PEG2000 and APA-PEG2000 at 1700 cm^{-1} which attributed to C=O stretching of COOH group. This observation confirms the partial esterification of MPA-PEG2000.



Figure(3.2) : IR spectra of a)-APA, b)MPA and c)MPA-PEG 600

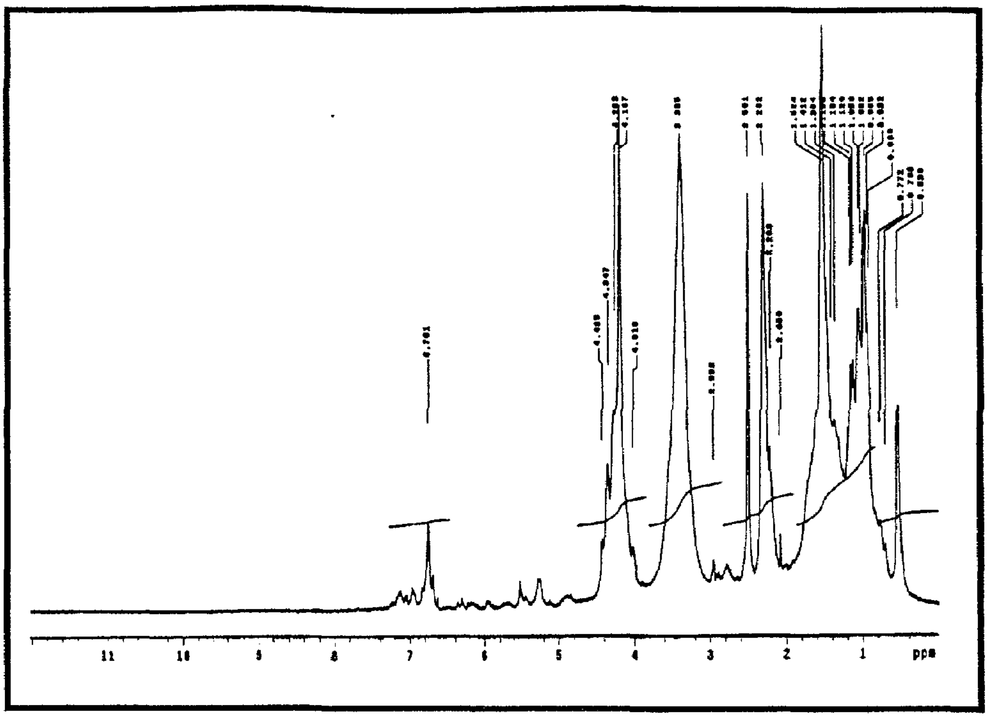
Furthermore, ^{1}HNMR analysis was used to confirm the structure of the prepared compounds. ^{1}HNMR spectra of both APA- PEG1000 and MPA-PEG1000 were presented in ***Figures (3.3 a&b)*** whereas that for APA-PEG-2000 is supplied herein in ***Figure (3.4).***

Careful interpretation to these spectra, the following chemical shifts can be noticed:

- The chemical shift at $\delta = 3.6$ ppm for protons of oxyethylene units
- The chemical shift at 2.4 or 2.6 ppm for OH proton of PEG.
- The chemical shift at 4.3 ppm which represented COO- CH_2

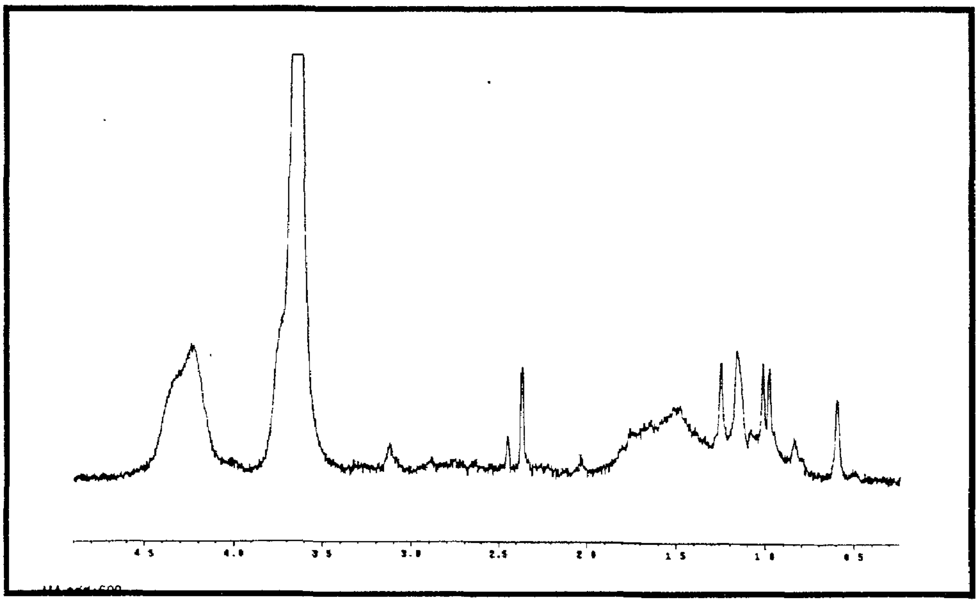
These peaks were observed in spectra of all surfactants. But there are some other characteristic peaks such as the chemical shift of methylene $(CH_2)_n$ of hydrophenancerene unit of rosin which appeared at $\delta = 1.35$ ppm and used to assign the incorporation of rosin in the structure of the prepared surfactants. Also, the -OH signal that usually appears at 10.3 ppm in spectrum of rosin and assigned for -COOH group is absent from spectra of APA-PEG600, APA-PEG1000, MPA-PEG 600 and MPA-PEG1000 surfactants. While this signal is very obvious in APA-

PEG2000 and MPA-PEG 2000 spectra. This observation certainly indicates that the carboxylic groups of adducts were completely esterified with PEG600 and PEG1000 and partially esterified with PEG2000. Moreover, the integration area of terminal PEG-OH signal appeared at 2.3 ppm was compared to the integration area of -COOH signal, 10.3ppm, to determine the degree of esterification of adducts with PEG-2000 and to calculate the theoretical molecular weight of the prepared surfactants. The ^{1}HNMR spectra of MPA-PEG2000 and APA-PEG2000 indicate that only one from two -COOH groups of MPA and APA were esterified.



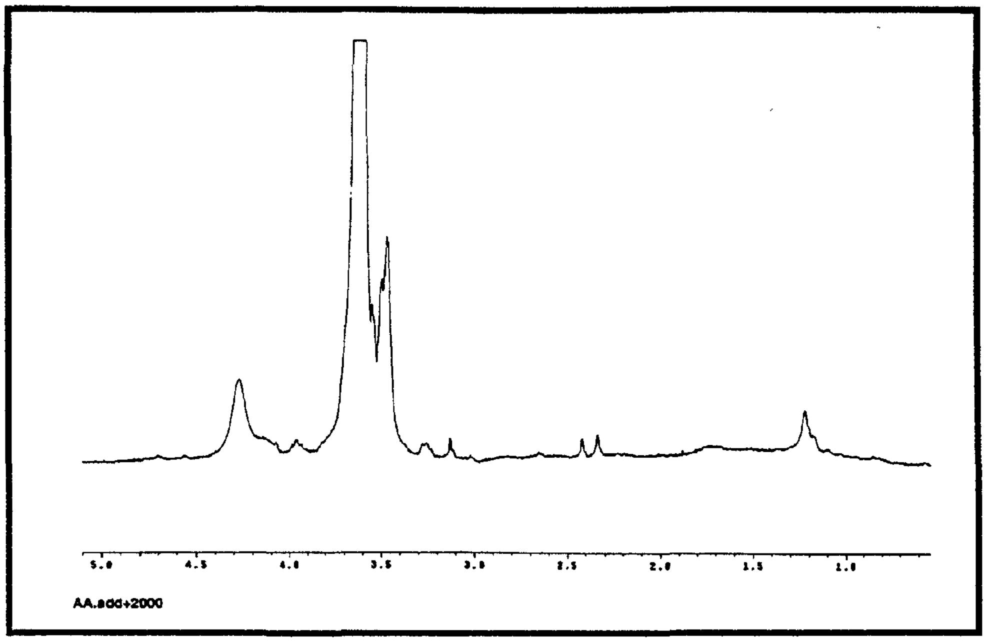
Chemical shifts (ppm)

Figure (3.3a): ^{1}HNMR Spectrum of APA-PEG-1000



Chemical shift (ppm)

Figure (3.3b): ^{1}HNMR Spectrum of MPA-PEG-1000



Chemical shift (ppm)

Figure (3.4): ^{1}HNMR Spectrum of APA-PEG-2000

3.1.2. Preparation of Nonionic Surfactants from Hydroxyl Derivatives of Rosin Acids

Rosin has been recognized to have excellent solubility with organic solvents and its compatibility with a variety of other synthetic resins. This is because rosin acids have a hydrophobic skeleton in combination with hydrophilic carboxy groups. It is advantageous to modify these rosin acids for many applications. In the present work modification of rosin acid to di-and polyhydroxyl derivatives are completed through different methods which can be described in the following section. There are isomeric forms of rosin acids. These isomers including abietic, levopimaric, palustric, neoabietic, dehydroabietic, dihydroabietic and tetrahydroabietic acids **[Chen (1992)]**.

The present work deals with synthesis of nonionic surfactants by reacting of rosin acid with FA at different temperatures followed by reacting the carboxylic moiety of rosin acid with PEG having different molecular weights 600, 1000 and 2000 g/mol. The scheme of synthesis was represented in ***Figure*** *(3.5)*. The scheme also shows synthesis of trimethylol derivatives of rosin acid and their condensation with FA. The proposed structure of condensed product at temperature up to 90 °C (RFA) indicated that the trimethylol of rosin acid can be formed with molar ratio of 1: 3 (for rosin acid : FA molar ratio). The physico-chemical properties of the produced hydroxyl derivative of rosin such as acid number (mg KOH/g of resin), melting point (°C) and molecular weight (g/mol) were 140, 111 and 756, respectively.

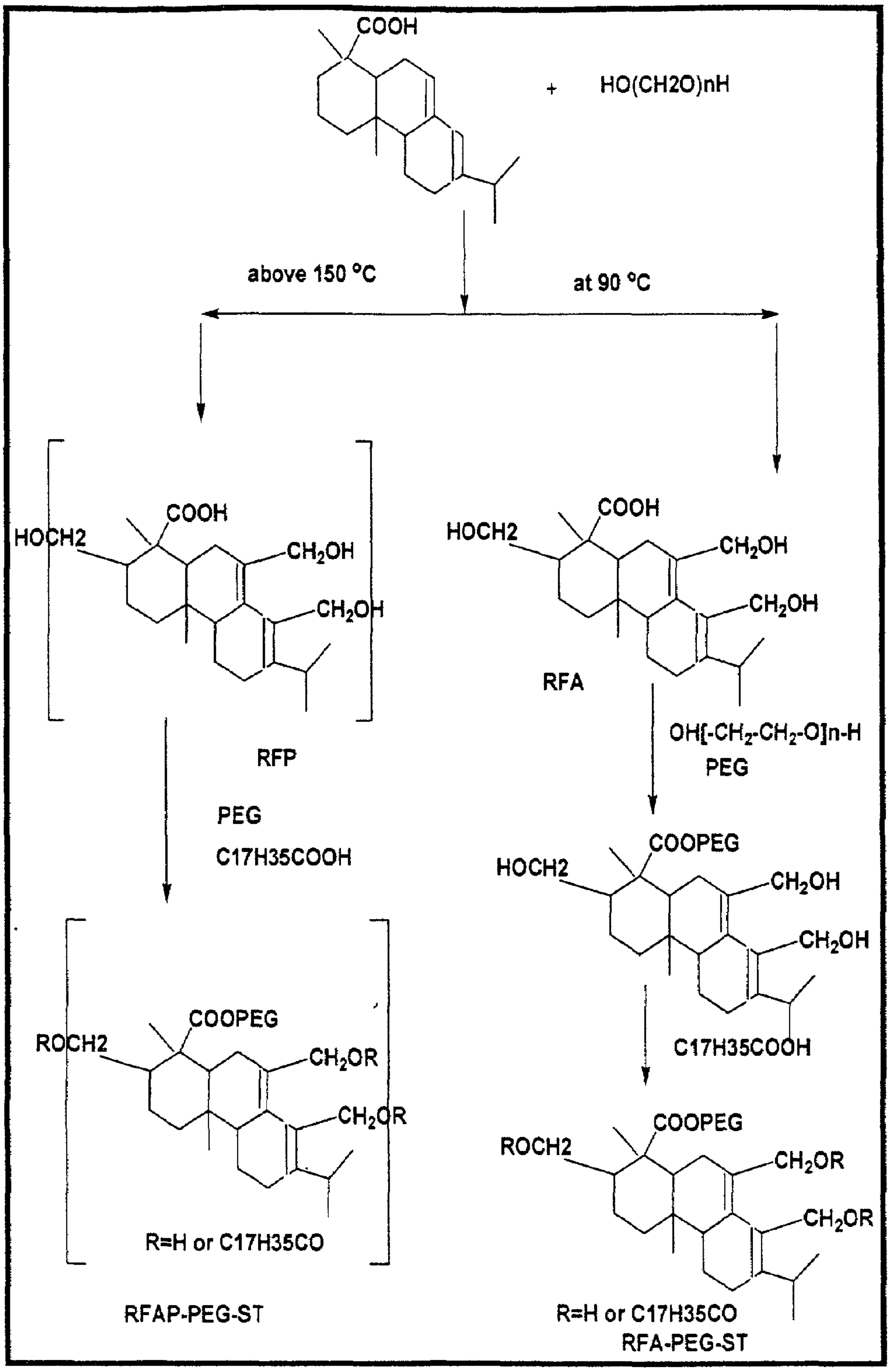


Figure (3.5): Scheme of Synthesis of RFA-PEG and RFAP-PEG Surfactants

The value of acid number indicates that the carboxylic groups of rosin acid are not participating in the condensation reactions. It was previously reported that **[Atta et.al. (1997)]**, the resins synthesized by the polycondensation of rosin acid with FA at temperature up to 150°C release few quantities of water and carbon dioxide when the reaction is continued at high temperature (up to 240°C). The resin formed by the condensation of rosin acid with FA (molar ratio 3) at high temperature (RFAP) was represented in ***Figure (3.5)***. The physico-chemical properties of the produced rosin are: acid number (mg KOH/g of resin), melting point (°C) and molecular weight (g/mol) were 90, 75 and 1690, respectively. The lower acid value of the condensed resin at high temperature indicates the partial participation of carboxylic groups in the condensation reaction. This observation agrees with the data of condensation of abietic acid with FA at high temperature **[Atta and Arndt (2002)]**.

As mentioned earlier, the present work aims to synthesize polymeric surfactants as oil spill dispersants. This was achieved by reaction of a carboxylic group, monohydroxyl, dihydroxyl- or trihydroxyl derivatives of rosin formaldehyde derivatives through esterification with PEG and stearic acid (ST). The esterification of RFA and RFAP with PEG was used to increase hydrophilicity of rosin acids. The notation of the synthesized surfactants was mentioned in the experimental section.

Furthermore, RFAP was reacted with PEG of different molecular weights to produce number of nonionic surfactants. The chemical structure of the produced surfactants was confirmed by using IR spectroscopy. It was observed that the spectra of all RFA-PEG derivatives are nearly identical. Accordingly, representative infrared spectral patterns of RFA-PEG1000 and RFA-PEG2000-ST were represented in ***Figure (3.6 a&b)*** respectively to compare between the bands appear in absence and presence of ST. Careful inspection to the above mentioned Figures, the following bands can be detected:

- The stretching band at 1745 cm^{-1} for carbonyl (C=O) of ester.
- The stretching band at 1100 cm^{-1} for C-O of ether.
- The band at 3450 cm^{-1} for OH stretching.

These bands are observed in all spectra. On the other hand, the IR spectrum of RFA-PEG2000-ST ***Figure (3.6 b)*** shows the appearance of band at 721 cm^{-1} (which is attributed to $C-(CH_2)_n-C$ bending vibration of the long alkyl chain moiety of the ST ester). This band confirms the incorporation of ST.

Further confirmation for the chemical structure of RFA-PEG1000 and RFA-PEG2000ST surfactants was obtained by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of the aforementioned surfactants are represented in ***Figure (3.7a&b).*** The disappearance of peak at 5.1 ppm, which attributed to protons of conjugated diene of rosin acid, and appearance of new peak at 2.5 ppm indicates the addition of CH_2OH group on olefinic protons. The protons of oxyethylene units at $\delta = 3.6$ ppm, –OH proton of PEG at δ 2.5 ppm, were observed in the spectra. The confirmation of incorporation of ST group into the chemical structure of RFA-PEG-ST was assigned by the following peaks:

- CH_3 and $COOCH_2$ protons of ST appeared as an intense peaks at δ 1.35 and 3.85 ppm.
- The Signals of methylene $(CH_2)_n$ of ST and hydrophenancerene groups, appeared as an intense broad peaks at δ 1.35 was used to assign the incorporation of aliphatic ST and rosin in the structure of the prepared surfactants.

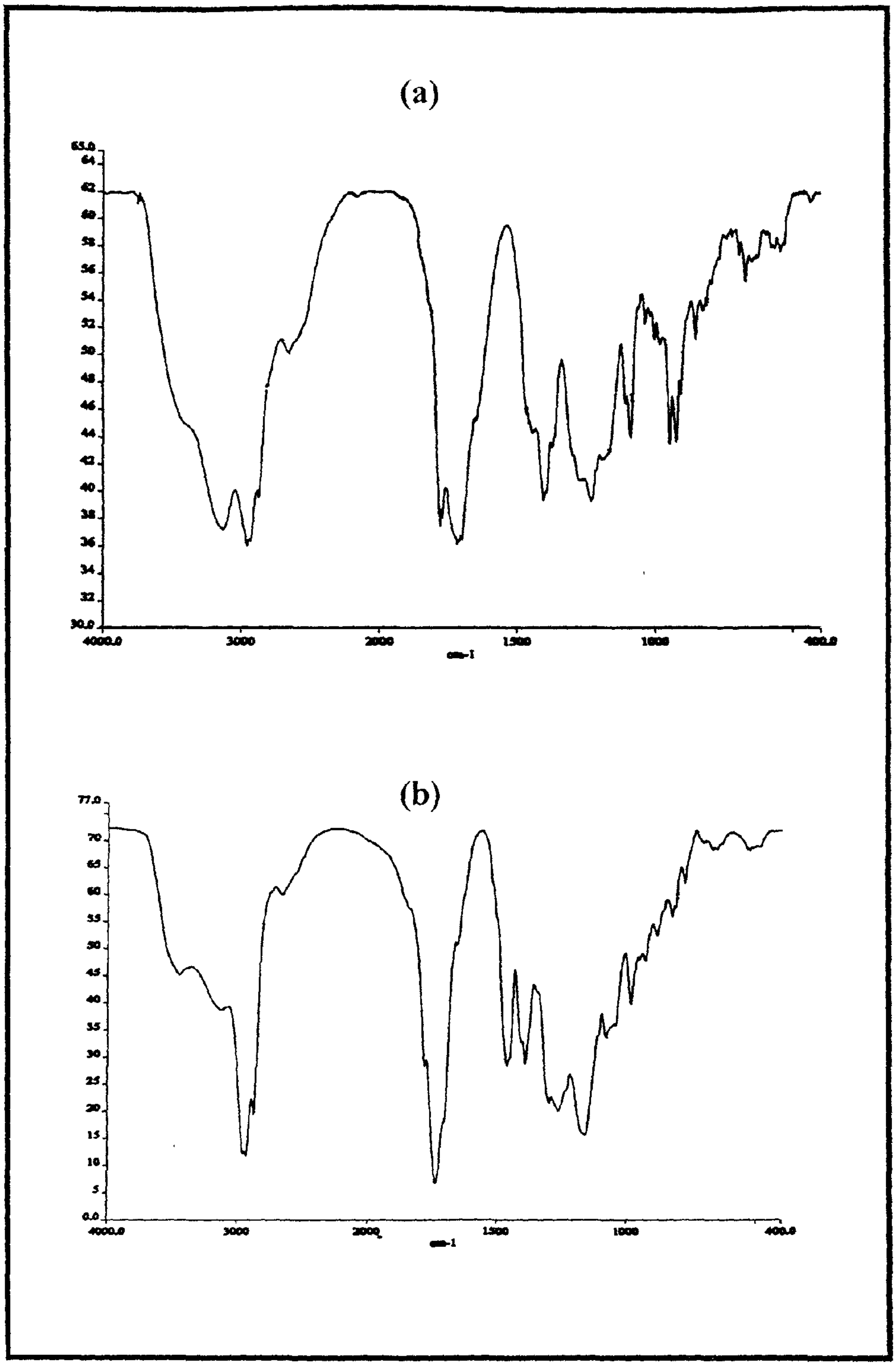


Figure (3.6): IR spectra of a) RFA-PEG1000 and b)RFA-PEG2000-ST

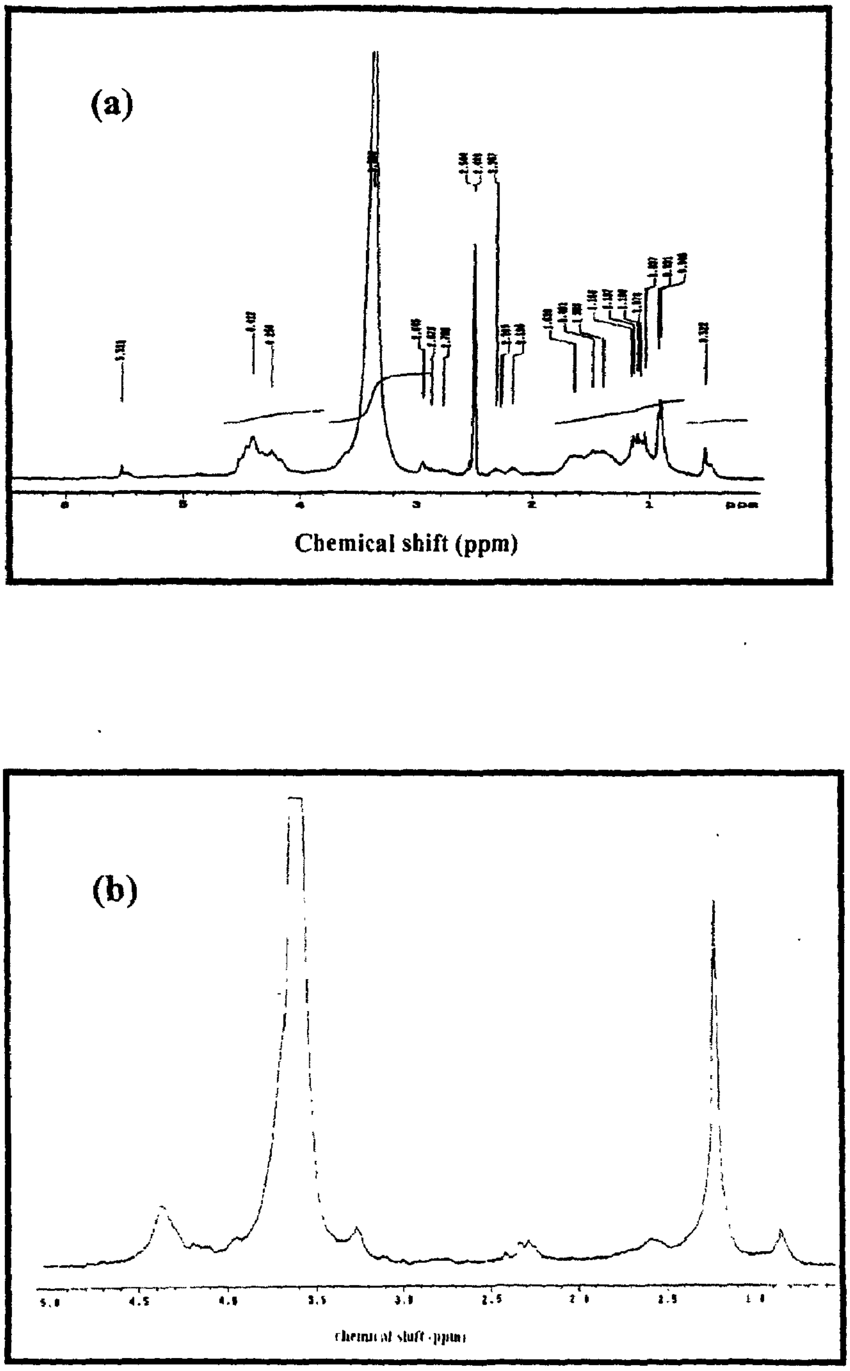


Figure (3.7): ^{1}HNMR Spectra of a) RFA-PEG1000 & b) RFA-PEG2000ST

3.2. SOLUBILITY AND SURFACE PROPERTIES OF THE PREPARED SURFACTANTS

It is well known that the modification of polymer backbone certainly affect inter- and intramolecular interactions. The change in these interactions yields different hydrophobicity, chain flexibility and solubility. Accordingly, the selection of the proper solvent depends to a large extent on the type and quantity of the branches attached to the backbone. In this respect, the prepared surfactants based on rosin oligomers are soluble in cold or hot water. The solubility and state of polymer solutions depend on the backbone composition and hydrogen bonds between polar groups of modified rosin. Consequently, because of different types of interactions, the solution behaviors of rosin surfactants are difficult to predict. On the other hand when they concentrate at the surface and orient their lyophobic groups away from the solvent, the free energy of solution is minimized.

However, there are some other means of minimizing the free energy in the systems. The distortion of the solvent structure can also be decreased (and the free energy of the solution reduced) by the aggregation of the surface-active molecules into clusters (micelles) while their hydrophilic groups directed toward the solvent. The micellization is therefore a mechanism alternative to adsorption at the interfaces for removing the lyophobic groups from contact with the solvent, thereby reducing the free energy of the system. Classical equations derived by Griffin and Davies were used to calculate the HLB number of surfactants **[Griffin (1949)]**, however, these equations consider only the chemical compositions, and the effect of position isomerism is not taken into account. Because HLB is difficult to determine experimentally, the cloud point of the prepared surfactants was used to represent the hydrophile–lipophile balance. This phenomenon can be explained from measuring of the cloud temperatures of the prepared surfactants solutions in water. It was established that aqueous solutions of polyoxyethylenated nonionics having oxyethylene content below about 80%, become turbid on being heated at a temperature known as the cloud point, above which there is a separation of the solution into two phases.

This phase separation occurs at a narrow temperature range (fairly constant) for surfactant concentrations below a few percent **[Synder (1971)]**. The phase appears to consist of an almost micelle-free dilute solution of the nonionic surfactant at a concentration equal to its critical micelle concentration (CMC). The temperature at which clouding occurs depends on the structure of the polyoxyethylenated nonionic surfactant. The cloud point is the temperature below which a single phase of molecular or micellar solution exists; above the cloud point the surfactant loses sufficient water solubility and a cloudy dispersion results. Above this temperature, the surfactant also ceases to perform some or all of its normal functions. So cloud point can be used to limit the choice of nonionic surfactants for application in certain processes.

A suggestion was made to regard the cloud point in solution of nonionic surfactant as a pseudo-phase inversion. For polyoxyethylene-type surfactant, the cloud point and the phase inversion temperature (PIT) are directly correlated when surfactant alone is dispersed in water. PIT is defined as the temperature at which the hydrophile–lipophile property of surfactant just balances at the interface **[Nakagawa and Shinoda (1963)]**. A study on the effect of structural changes in the surfactant molecule on its cloud point **[Schott (1969)]** indicates that, at constant oxyethylene content the cloud point is lowered due to decreased molecular weight of the surfactant and increasing length of the hydrophobic group. The solubility of the prepared surfactants depends on the method of purification.

However, the modified rosin and PEG polymers have dissimilar solubility properties. This difference in solubility is due to the difference in hydrophil-lipophil balance (HLB) of the surfactants. The solubility of the prepared nonionic surfactants, based on PEG, in water, depends on the content and molecular weight of PEG, for instance, it was found that the nonionic surfactants based on rosin containing PEG with molecular weight 400 are of a lower limit for water solubility. The HLB values were calculated by using the general formula for nonionic surfactants, $HLB = [M_H / (M_H + M_L)] \times 20$, where M_H is the formula weight of the hydrophilic portion of the surfactant molecule and M_L is the formula weight of the hydrophobic portion. HLB values of nonionic surfactants based on modified water soluble rosin were calculated and listed in ***Tables (3.2 &3.3).***

The data mentioned that the prepared surfactants have different HLB values varied from 11-17 which indicate that the prepared surfactants have good solubility in water. It is also obvious that the APA surfactants have lower HLB values than MPA adducts which can be attributed to that the structure of APA surfactants is more hydrophobic.

Table (3.2): Surface Activity Based on MPA and APA Adducts at Different Temperature

Designation	M.Wt^1. (g/mol)	Cloud point	HLB	Surface Property	Temperature (K)			
					293	303	313	323
MPA-PEG600	2146	78^{0}C	16.7	^{2}CMC x 10^4	3.2	1.6	0.82	0.41
				$^3\gamma_{CMC}$	39	37	35	33
MPA-PEG1000	3346	83^{0}C	17.9	^{2}CMC x 10^4	2.5	0.67	0.31	0.16
				$^3\gamma_{CMC}$	37.5	34.8	33.9	31.2
MPA-PEG2000	4364	87^{0}C	18.3	^{2}CMC x 10^4	0.67	0.33	0.16	0.082
				3γ_{CMC}	40.5	39.5	36.9	35
APA-PEG600	1511	72^{0}C	15.8	^{2}CMC x 10^4	5.5	2.7	1.3	6.7
				3γ_{CMC}	35.4	34.4	34	33.1
APA-PEG1000	2311	75^{0}C	17.3	^{2}CMC x 10^4	1.2	0.61	0.304	0.167
				3γ_{CMC}	36.1	35.3	34.8	33
APA-PEG2000	2329	80^{0}C	18.1	^{2}CMC x 10^4	11	5.5	2.7	1.3
				3γ_{CMC}	39.1	37.1	35.2	33

^{1} Calculated from ^{1}HNMR analysis, ^{2} CMC x10^4 in (mol dm^{-3}), $^3\gamma_{CMC}$ in (mNm^{-1})

Table (3.3): Surface Activity Based on RFA and RFAP Adducts at Different Temperatures

Designation	M.Wt^{1}. (g/mol)	Cloud point	HLB	Surface Property	Temperature (K)			
					293	303	313	323
RFA-PEG600	982	75	12.2	^{2}CMC x 10^{4}	27	13.6	6.7	3.3
				$^{3}\gamma_{CMC}$	36.3	35.3	34.3	34
RFA-PEG1000	1382	79	14.4	^{2}CMC x 10^{4}	9.1	4.5	2.4	1.2
				$^{3}\gamma_{CMC}$	36.4	36.2	35.9	34.1
RFA-PEG2000	2382	82	16.7	^{2}CMC x 10^{4}	1.3	6.7	3.36	0.16
				$3\gamma_{CMC}$	36.1	34	33	32
RFA-PEG1000-ST	1666	77	12.1	^{2}CMC x 10^{4}	8.2	4.09	2.03	1.01
				$3\gamma_{CMC}$	37.8	36.4	34.9	33.2
RFA-PEG2000-ST	2666	80	15	^{2}CMC x 10^{4}	1.3	0.67	0.33	0.16
				$3\gamma_{CMC}$	37.3	36	35	34
RFAP-PEG2000		75	13	^{2}CMC x 10^{4}	2.7	1.3	0.67	0.33
				$3\gamma_{CMC}$	36	35	34.1	32.1
RFAP-PEG2000-ST		70	11	^{2}CMC x 10^{4}	5	1.23	0.61	0.30
				$3\gamma_{CMC}$	34.9	33.4	33	32.1

[1] Calculated from ^{1}HNMR analysis, [2] CMC x10^{4} in (mol dm^{-3}), $^{3}\gamma_{CMC}$ in (mNm^{-1})

The data listed in ***Table (3.3)*** indicated that surfactants based on RFAP have low HLB value when compared with RFA based surfactants. This can be attributed to the greater hydrophobicity of RFAP based surfactants due to polymerization of CH_2OH groups.

The cloud temperatures of the prepared surfactants were also listed in ***Tables (3.2) and (3.3).*** It was observable that the cloud points were progressively increased with elongating the length of the hydrophilic side chains. A study on the effect of structural changes in the surfactant molecule on its cloud point **[Schott (1969)]** indicated that, at constant oxyethylene content the cloud point is lowered due to the following reasons:

- Decreased molecular weight of the surfactant,
- Branching of the hydrophobic group,
- More central positions of the polyoxyethylene hydrophilic group in the surfactant molecule,
- replacement of terminal – OH methoxyl and
- Replacement of the ether linkage between the hydrophilic and hydrophobic group by an ester linkage.

The data listed in ***Tables (3.2 &3.3)*** agrees in harmony with the previous findings. It can be observed that the cloud point decreases with incorporation of ST in the prepared

RFA-PEG surfactants and with decreasing the molecular weight of PEG. This observation can be attributed to increasing the hydrophobic characteristics of the prepared surfactants. On the other hand, careful inspection to the data indicate that the cloud point of MPA adduct surfactants was higher than that determined for APA surfactants which correlated to high HLB values of MPA surfactants. Accordingly, the prepared MPA-PEG surfactants were highly water soluble surfactants than APA-PEG surfactants.

The micellization and adsorption behaviors of surfactants are based on the surface characteristics and the critical micelle concentrations (CMC). They were determined by the surface balance method. The CMC values of the prepared polymeric surfactants were determined at 293, 303, 313 and 323K from the change in the slope of the plotted data of surface tension (γ) versus the natural logarithm of the solute concentration. The relation was represented as adsorption isotherms and plotted in ***Figures (3.8-3.12)***. These were used for estimating surface activity and confirming the purity of the studied surfactants. It is of interest to mention that all obtained isotherms showed one phase, which is as an indication on the purity of the prepared surfactants. The obtained values of CMC for nonionics at different temperatures are tabulated in ***Tables (3.2&3.3)***, together with values for the surface tension at CMC. Generally, increasing the number of ethylene oxide units increases CMC values **[Bharadwaj & Hartland (1994)]** due to increasing the hydrophilicity and the solubility of the surfactants in water. Such improved solubility lowers the tendency for the surfactant to form micelles. Some investigators **[Beher(1958) and Carless et al.(1964)]** found that increasing of PEG units decreases CMC. However, those surfactants have very long hydrophobic tails (at least 16 carbons) and relatively low ethylene oxide units (EO is about 6-19). It may be possible in these cases that the low water solubility of these surfactants is due to the alkyl chain, not the EO chain.

Other investigators **[Atta (1999) , Al-Sabagh & Atta (1999), Atta & Arndt(2001) and Abdel Azim& Atta(2002)]** explain this behavior on the basis of coiling of the polyethylene oxide chains.

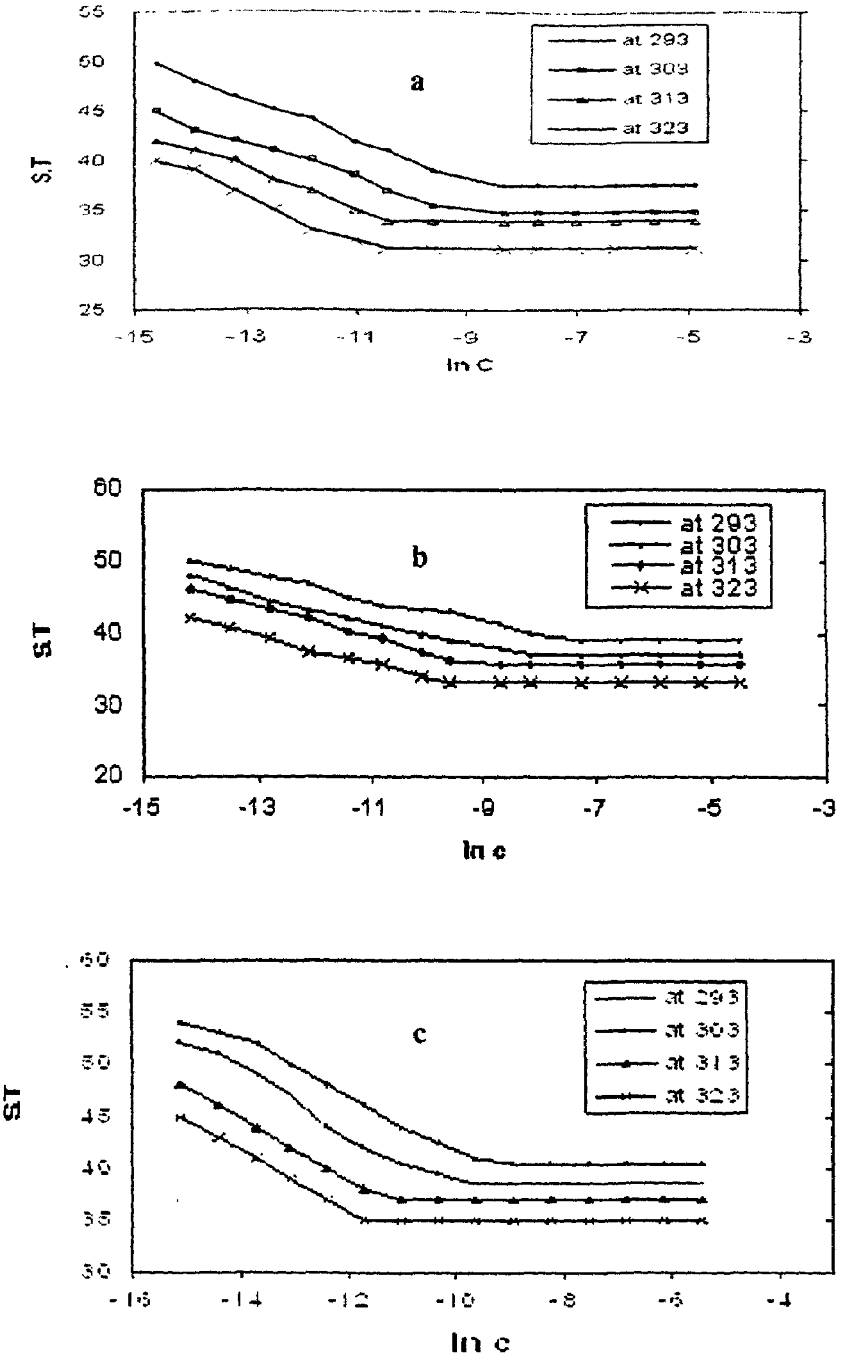


Figure (3.8): Surface tension-concentration Isotherms of a) MPA-PEG600,b)MPA-1000 and c)MPA 2000

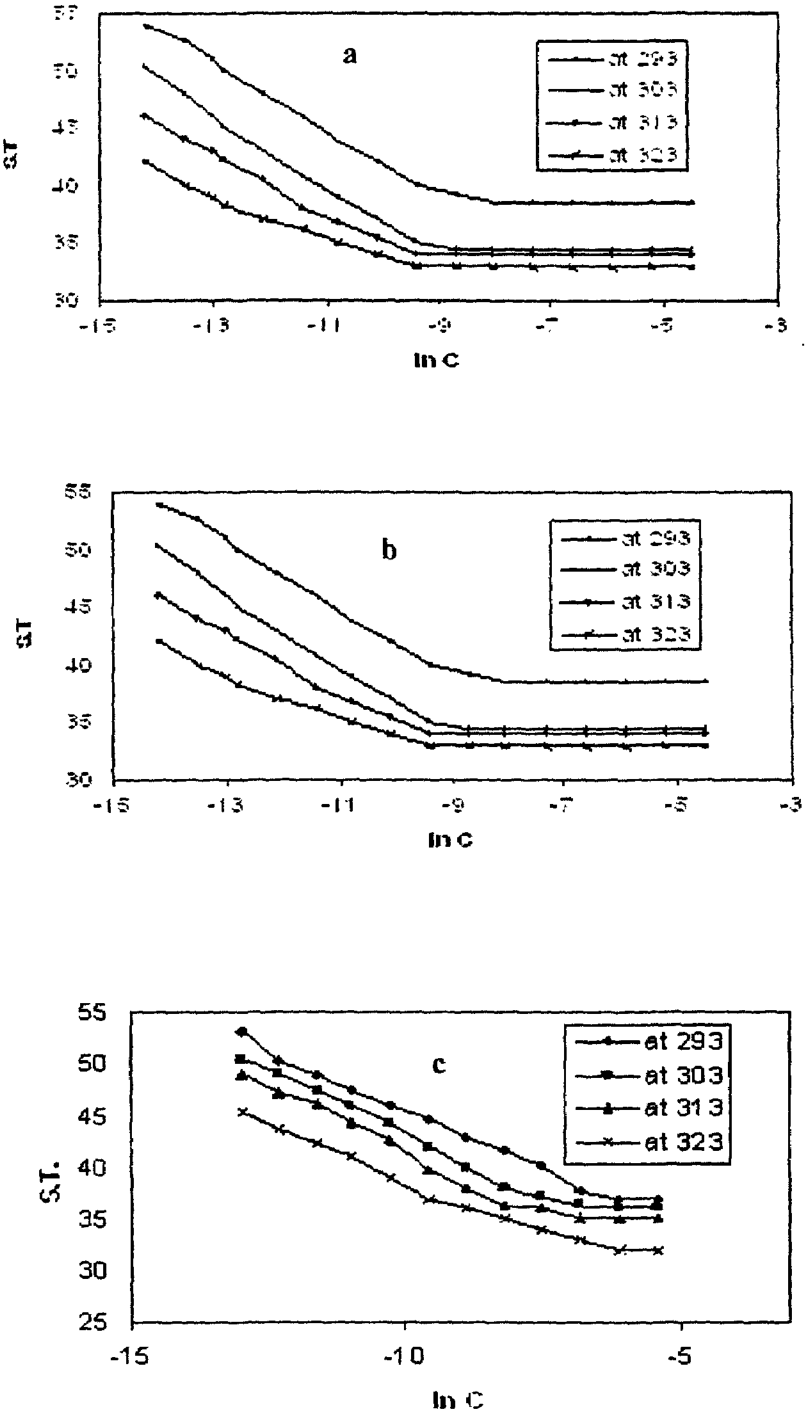


Figure (3.9): Surface tension-concentration Isotherms of a)APA-PEG600, B)APA-1000 C)APA-2000

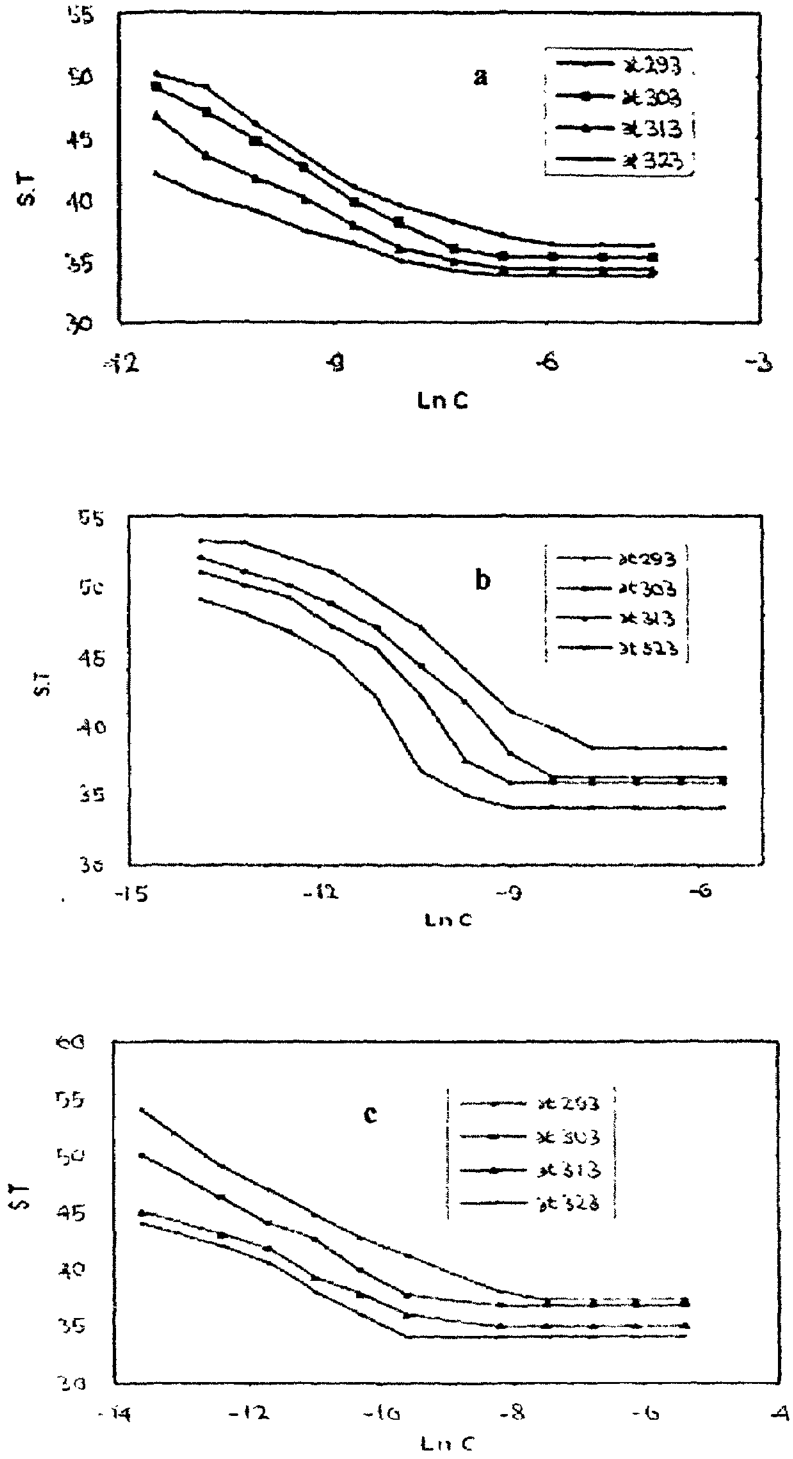
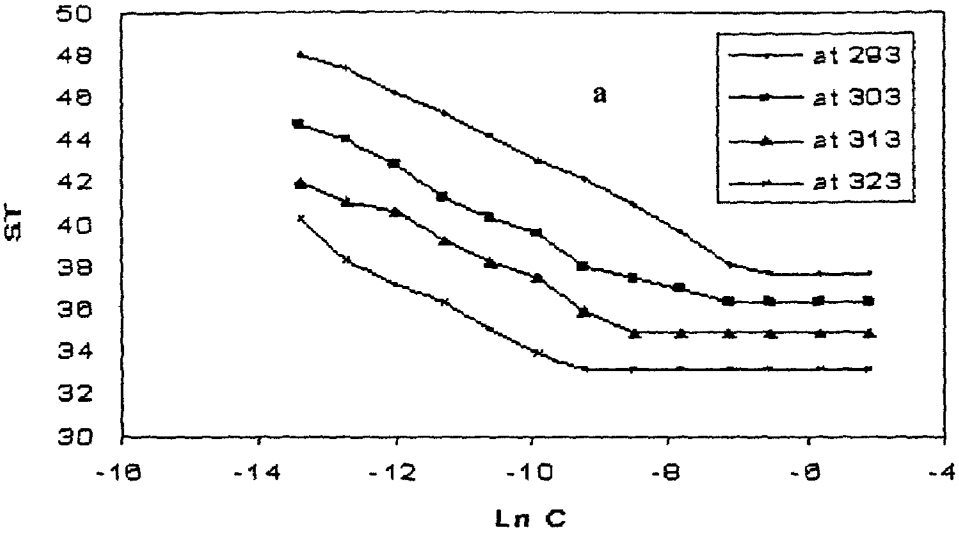


Figure (3.10): Surface tension-concentration Isotherms of a)RFA-PEG600, B)RFA-1000 and C)RFA-2000



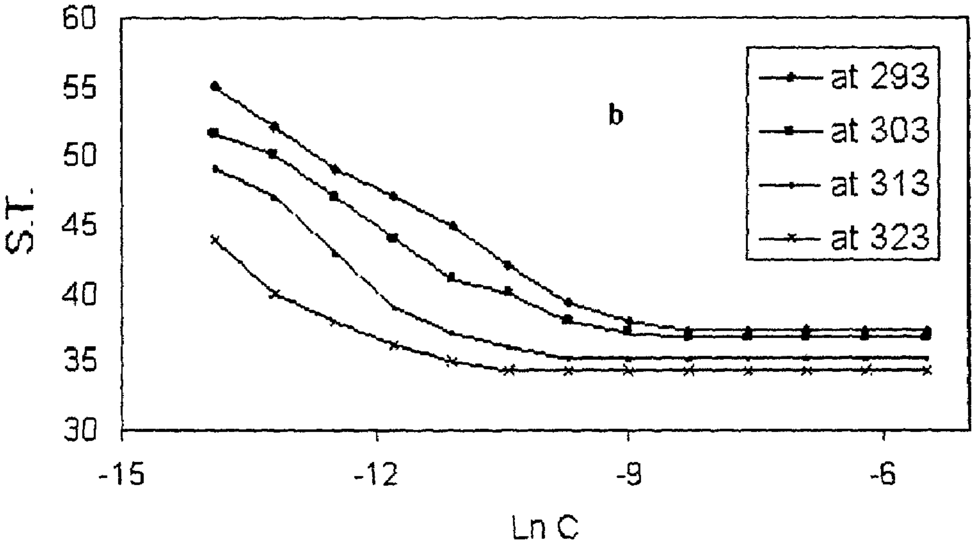


Figure (3.11): Surface tension-concentration Isotherms of RFA

a) 1000ST & b) 2000ST

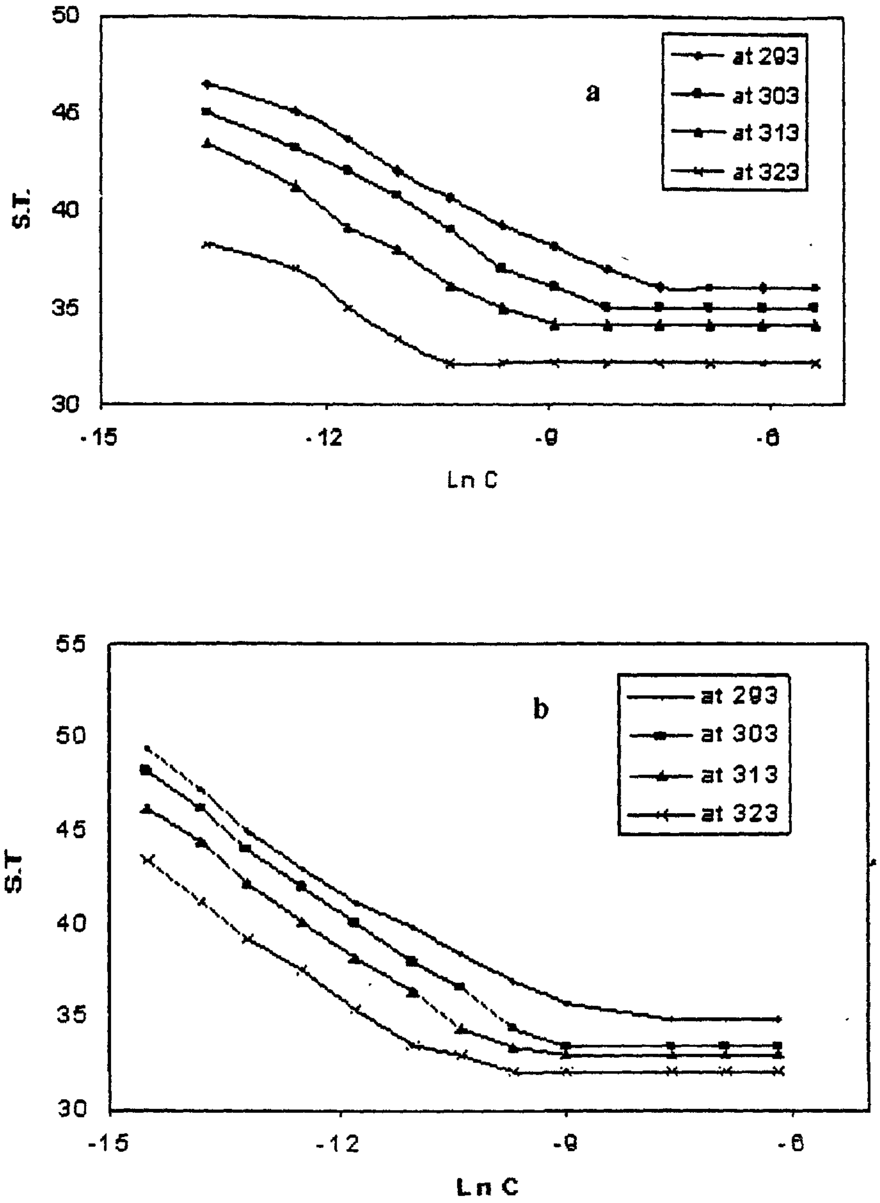


Figure (3.12): Surface tension-concentration Isotherms of a)RFAP- 2000 & b) RFAP-2000ST

In the present system, it was found that the CMC values of RFA-PEG, RFAP-PEG, MPA-PEG and APA-PEG surfactants are directly correlated to the number of oxyethylene groups in the molecule. This can be attributed to increase the formation of hydrogen bondings between high molecular weight of PEG moieties and water. On the other hand, it was observed that, the CMC values for RFA-PEG-ST decreased with increasing the molecular weight of PEG. This may be attributed to the hydrophobic interaction between ST groups which causes coiling of terminated polyethylene oxide. It was mentioned that the solubility of surfactants in water is controlled mainly by the structure of hydrophobic groups **[Al-Sabagh (1998)]**.

It was also observed that the incorporation of ST in both RFA-PEG1000 and RFA-PEG2000 surfactants decreases CMC values. This can be referred to increase hydrophobicity of surfactant with incorporation of hydrophobic groups. It is of interest to mention that the CMC for the same surfactant decreases with increasing the temperature. This may be attributed to the increase in the radius of gyration of the molecule as a result of increasing the temperature **[Abdel Azim (1995 &1996)]**.

Upon comparing the performance of surfactants at different interfaces it is usually necessary to distinguish between the amount of surfactant required to produce a given amount of change in the phenomena under investigation and the maximum change in the phenomenon that the surfactant can produce, regardless of amount used. The former parameter is the efficiency of the surfactant and the latter is its effectiveness. These two parameters do not necessarily run in parallel to each other in surfactants and in fact in many cases they run counter to each other. The direct determination of the amount of surfactant adsorbed per unit area of liquid-gas or liquid-liquid interface, although possible, is not generally considered because of the difficulty of isolating the interfacial region from the bulk phase for purpose of analysis when the interfacial region is small, and of measuring the interfacial area when it is large. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from surface or interfacial tension measurements. As a result, a plot of surface (or interfacial) tension as a function of equilibrium, concentration of surfactant in one of the liquid phases, rather than an adsorption isotherm, is generally used to describe adsorption of this interface can readily be calculated as surface excess concentration Γ_{max}. The surface excess concentration of surfactant at the interface may therefore be calculated from surface or interfacial tension data by using the following equation:

$$\Gamma_{\max} = \frac{1}{RT}\left(\frac{-\partial\gamma}{\partial \ln c}\right)_T \qquad \textbf{(3.1)}$$

Where $\left(\frac{-\partial\gamma}{\partial \ln c}\right)_T$ is the slope of the plot of γ versus ln c at a constant temperature (T), and R is the gas constant in $\mathrm{Jmol^{-1}K^{-1}}$. The surface excess concentration at surface saturation is a useful measure of the effectiveness of adsorption of surfactant at the liquid-gas or liquid-liquid interface, since it is the maximum value which adsorption can attain.

The $\Gamma_{\max}$ values were used for calculating the minimum area $A_{\min}$ at the aqueous-air interface. The area per molecule at the interface provides information on the degree of the packing and the orientation of the adsorbed surfactant molecules, when compared with the dimensions of the molecule as obtained by use of models. From the surface excess concentration, the area per molecule at interface is calculated using ***equation (3.2)***.

$$A_{\min} = \frac{10^{16}}{N\Gamma_{\max}} \qquad (3.2)$$

Where N is Avogadro's number.

The $\Gamma_{\max}$, $A_{\min}$ and π_{CMC} values were calculated ***and listed in Tables (3.4&3.5).*** The variation of $A_{\min}$ values of nonionic surfactants can be attributed to the fact that there are two kinds of behaviors can be suggested for this variation by regarding the area occupied per molecule as follows:

1. The nonionic surfactants with hydrophobic groups at opposite ends of the molecule show large $A_{\min}$ at the interface and are probably lying flat at the interface, making it easier for ester group interaction at interface; then the molecule occupies a bigger area.
2. The nonionic surfactants have ended with two hydrophilic groups, the easier for packing at the interface, thus obstructing the main chain interaction at the interface; then, the molecule occupies a smaller area, i.e., adsorption.

The data, listed in ***Tables (3.4&3.5)*** show that the minimum areas per molecule at the aqueous solution / air interface increases with increasing the number of oxyethylene units in the molecule of MPA-PEG, APA-

PEG, RFA-PEG and RFAP-PEG surfactants. This behavior can be referred to the interaction of surfactant molecule with water at interface.

It was also observed that the A_{min} of the surfactants based on MPA adduct is higher than that based on APA surfactants. This can be attributed to that the nonionic surfactants based on APA have low PEG contents than MPA adducts which reflects the easier for packing at the interface; then the molecule occupies a smaller area, i.e., APA adducts posses higher adsorption at interface than that based on MPA adduct.

Table (3.4): Surface Properties of the Surfactants Based on MPA and APA Surfactants at Different Temperatures

Designation	Surface property	Temperature (K)			
		293	303	313	323
MPA-PEG600	Γ_{max} x 10^{10}(mol cm^{-2})	0.78	0.76	0.75	0.74
	A_{min} (nm^2/molecule)	0.213	0.215	0.218	0.220
	Π_{CMC}(mNm^{-1})	33.8	36.7	35.1	36.5
	pC20	6.3	6.7	7	8.5
MPA-PEG1000	Γ_{max} x 10^{10}(mol cm^{-2})	0.8	0.67	0.75	0.93
	A_{min} (nm^2/molecule)	0.2	0.24	0.22	0.17
	Π_{CMC}(mNm^{-1})	35.3	36.9	37.1	38.3
	pC20	7.08	7.73	9.3	9.3
MPA-PEG2000	Γ_{max} x 10^{10}(mol cm^{-2})	0.9	0.99	1.1	1.1
	A_{min} (nm^2/molecule)	0.18	0.16	0.15	0.15
	Π_{CMC}(mNm^{-1})	32.2	33.2	33.7	34.5
	pC20	5.7	6.25	7.17	8
APA-PEG600	Γ_{max} x 10^{10}(mol cm^{-2})	1.3	1.2	0.74	0.79
	A_{min} (nm^2/molecule)	0.12	0.13	0.21	0.24
	Π_{CMC}(mNm^{-1})	37.4	37.3	36.6	36.4
	pC20	6.30	6.73	7.00	8.50
APA-PEG1000	Γ_{max} x 10^{10}(mol cm^{-2})	0.77	0.80	0.68	0.63
	A_{min} (nm^2/molecule)	0.21	0.20	0.24	0.26
	Π_{CMC}(mNm^{-1})	36.7	36.4	35.8	34.5
	pC20	7.08	7.73	9.3	9.3
APA-PEG2000	Γ_{max} x 10^{10}(mol cm^{-2})	0.57	0.39	0.76	0.59
	A_{min} (nm^2/molecule)	0.29	0.42	0.218	0.28
	Π_{CMC}(mNm^{-1})	33.7	34.6	35.4	36.5
	pC20	5.7	6.25	7.17	8.00

Table (3.5): Surface Properties of the Surfactants Based on RFA and RFAP Surfactants at Different Temperatures

Designation	Surface property	Temperature (K)			
		293	303	313	323
RFA-PEG600	Γ_{max} x 10^{10}(mol cm^{-2})	1.3	1.2	1.1	0.7
	A_{min} (nm^2/molecule)	0.12	0.13	0.15	0.23
	Π_{CMC}(mNm^{-1})	36.5	36.4	36.4	35.5
	pC20	5.3	5.5	5.6	6.8
RFA-PEG1000	Γ_{max} x 10^{10}(mol cm^{-2})	0.8	0.87	0.9	0.7
	A_{min} (nm^2/molecule)	0.207	0.19	0.18	0.23
	Π_{CMC}(mNm^{-1})	34.4	35.5	34.7	35.4
	pC20	5.26	5.6	5.7	6.13
RFA-PEG2000	Γ_{max} x 10^{10}(mol cm^{-2})	0.9	0.93	0.78	0.63
	A_{min} (nm^2/molecule)	0.18	0.17	0.21	0.26
	Π_{CMC}(mNm^{-1})	36.7	37.7	37.6	37.53
	pC20	5.4	5.8	6.4	6.78
RFA-PEG1000-ST	Γ_{max} x 10^{10}(mol cm^{-2})	0.5	0.57	0.56	0.56
	A_{min} (nm^2/molecule)	0.33	0.29	0.297	0.297
	Π_{CMC}(mNm^{-1})	35	35.5	35.7	36.3
	pC20	6.8	7.5	7.5	8.17
RFA-PEG2000-ST	Γ_{max} x 10^{10}(mol cm^{-2})	0.62	0.59	0.58	0.63
	A_{min} (nm^2/molecule)	0.62	0.59	0.58	0.63
	Π_{CMC}(mNm^{-1})	35.5	35.7	35.6	35.5
	pC20	5.4	5.9	7	7.1
RFAP-PEG2000	Γ_{max} x 10^{10}(mol cm^{-2})	0.7	0.85	0.94	0.92
	A_{min} (nm^2/molecule)	0.23	0.19	0.17	0.18
	Π_{CMC}(mNm^{-1})	36.84	36.71	36.5	37.4
	pC20	6.6	6.7	7.17	8.13
RFAP-PEG2000-ST	Γ_{max} x 10^{10}(mol cm^{-2})	0.4	1.0	1.07	1.04
	A_{min} (nm^2/molecule)	0.13	0.16	0.15	0.15
	Π_{CMC}(mNm^{-1})	37	37.3	37.6	38.4
	pC20	6.47	6.6	6.9	7.43

The data of $A_{\min}$ and $\Gamma_{\max}$ indicates the dependence of the effectiveness of adsorption at the aqueous solution / air interfaces on the structure of surfactants.

It was found that incorporation of ST in the structure appears to have an unusual small increase in $A_{\min}$ at the interface. This can be attributed to that ST group makes coiling of hydrophobic chain with a relazation of PEG chains that consequent increases $A_{\min}$ **[Mukerjee(1967)].**

In polyoxyethylenated nonionics the lack of significant temperature effect may be resulted from two compensating effects: **[Crook et al.(1964)].**

- Decrease in $A_{\min}$ at the surface due to increased dehydration of the hydrophilic group at higher temperature.
- Increase in $A_{\min}$ as a result of enhanced molecular and thermal motion at higher temperature

Careful inspection of data, indicates that, $A_{\min}$ of the surfactants have two opposite relations with the temperature. The $A_{\min}$ may be increased or decreased with increasing the temperature. It was found that the minimum area per molecule also increases with increase in temperature, as would be expected from the increased thermal agitation of the molecules in the surface film.

The surface tension values at CMC were also used to calculate values of surface pressure (effectiveness). The effectiveness of surface tension reduction, $\pi_{CMC} = \gamma_o - \gamma_{CMC}$, where γ_o is the surface tension of water and γ_{CMC} is the surface tension of solution at CMC **[Tamaki (1967)]**, was determined at different temperatures.

It is expected that the most efficient surfactant is the one that gives the greater lowering in surface tension at its critical micelle concentration. The effectiveness increases with increasing the length of carbon chain in the hydrophobic moiety. The efficiency (PC_{20}) is determined by the concentration (mol dm^{-3}) capable to suppress the surface tension by 20 mN/m. The efficiency of the prepared surfactants as listed in, ***Tables (3.4&3.5)*** increases with decreasing molecular weight of PEG and with increasing temperature. The effectiveness of surface tension reduction, π_{CMC}, in these compounds shows a steady decrease with increase in the number of oxyethylene units. In polyoxyethylyenated nonionics, an increase in the number of oxyethylene units in the hydrophilic group above six units, in contrast to its large effect in decreasing the effectiveness of adsorption, seems to cause only a small decrease in the efficiency of adsorption. This appears to indicate a very small change in the free energy of transfer of the molecule from bulk phase interior to the interface with change in the number of EO above six in the hydrophilic head.

The effectiveness of adsorption, however, may increase, decrease or show no change with increase in the length of the hydrophobic group depending on the orientation of the surfactant at interface. If the surfactant is perpendicular to the surface in a close-packed arrangement, an increase in the length of the straight-chain hydrophobic group appears to cause no significant change in the number of moles of surfactant adsorbed per unit area of surface at surface saturation **[Tamaki (1967)]**. This is because; the cross-sectional area occupied by the chain oriented perpendicular to the interface does not change with increase in the number of units in the chain. It was previously deduced that the larger the hydrophobic group, the smaller the amount adsorbed at surface saturation **[Connor & Ottewill (1971)]**. If the arrangement is predominantly perpendicular but not close-packed, there may be some increase in the effectiveness of adsorption with increase length of hydrophobic group, resulting from greater Van der Waals attraction and consequent closer packing of longer chains

[Snyder (1968)]. Nonionic surfactants with short PEG chains show decrease in both efficiency and effectiveness **[Horig (1959), Kuno & Abe (1961) and Snyder (1968)]**. When the area of hydrophilic chain is greater than that of the hydrophobic group, the larger the hydrophilic chain, the smaller the amount adsorbed at surface saturation. However, if the orientation of the surfactant is parallel to the interface, the effectiveness of adsorption may be decreased with increasing the chain length and thus saturation of the surface will be accomplished by a smaller number of molecules **[Nagarajan & Ganesh (1989)].**

Finally,from data listed in tables(3.4-3.5), it can be concluded that the MPA and RFA show grater adsorption at air/water interface when compared to APA and RFAP surfactant.This can be attributed to the interaction between PEG units in the latter surfactants which decrease Γ_{max} and increase A_{min}.

3.3.THERMODYNAMIC PARAMETERS OF MICELLIZATION AND ADSORPTION

Amphiphilic block and graft copolymers consisting of hydrophilic and hydrophobic parts have become subjects of numerous studies on their solution and surface properties **[Riess et al. (1958), Glars (1971) and Tuzar & Kratochvil(1971)]**. These polymers are characterized by their ability to form micelles in water. There are two principally different models for micelle structure. A mean density model **[Leibler et al.(1983) and Nagarajan& Ganesh (1989)]** which is the most appropriate one for micelles consisting of a large core with relatively thin corona, and star model **[Halperin(1987)]** which is the most appropriate for those having a small core from which long chains protrude to form a large corona. The ability for micellization processes depends on thermodynamic parameters, (enthalpy ΔH, entropy ΔS and free energy ΔG) of micellization. The thermodynamic parameters of micellization are the standard free energies ΔG_{mic}, enthalpies ΔH_{mic}, and entropies ΔS_{mic}, of micellization for nonionic surfactants.

$$\Delta G_{mic}=RT\ln CMC \qquad (3.3)$$

Values of ΔS_{mic} were obtained from ***Eq (3.4)*** by invoking the values of ΔG_{mic} at 293, 303, 313 and 323K.

$$\frac{\partial \Delta G_{mic}}{\partial T} = -\Delta S_{mic} \qquad \textbf{(3.4)}$$

In addition, ΔH_{mic}, was calculated from ΔG_{mic} and ΔS_{mic} by applying ***equation (3.5).***

$$\Delta H_{mic} = \Delta G_{mic} + T\Delta S_{mic} \qquad \textbf{(3.5)}$$

The thermodynamic parameters values of adsorption, ΔG_{ad}, ΔH_{ad} and ΔS_{ad} were calculated via equations (3.6), (3.7) and (3.8), respectively **[Rosen & Aronson (1981)].**

$$\Delta G_{ad} = RT\ln CMC - 0.6023\Pi_{CMC}A_{min} \qquad \textbf{(3.6)}$$

$$\frac{\partial \Delta G_{ad}}{\partial T} = -\Delta S_{ad} \qquad \textbf{(3.7)}$$

$$\Delta H_{ad} = \Delta G_{ad} + T\Delta S_{ad} \qquad \textbf{(3.8)}$$

Detailed discussion for the thermodynamic parameters of micellization and adsorption for the prepared surfactants will be provided in next sections.

3.3.1. Thermodynamic Parameters of Micellization.

The values of ΔG_{mic}, ΔH_{mic} and ΔS_{mic} for nonionic surfactants are calculated and listed in ***Tables (3.6&3.7).*** Analyzing the thermodynamic parameters of micellization leads to the fact that micellization process is spontaneous ($\Delta G_{mic} < 0$). The data show that ΔG_{mic} value of MPA-PEG 2000 is more negative than other MPA-PEG and APA-PEG surfactants. This indicates that the increase of hydrophilic groups favors the micellization process, thus covering the most important requirement for surfactant detergency. It was also noted that ΔG_{mic} values are more negative with RFA-PEG-ST than RFA-PEG surfactants. On the other hand, the data reveal that $-\Delta G_{mic}$ increases with increasing temperature from 293 to 323K. The data listed in ***Tables (3.6&3.7)*** show that ΔS_{mic} values are all positive. This reflects the increased randomness in the system upon transformation of the nonionic surfactant molecules into micelles or increasing freedom of the hydrophobic chain in the nonpolar interior of the micelles compared to aqueous environment. The increment of positive ΔS_{mic} value with increasing the number of oxyethylene units in the surfactant molecule was initially by other investigators **[Riess et al. (1958) and Hudson & Pethica (1967)].**

Table (3.6): Thermodynamic Parameters of Micellization for Rosin Adducts Surfactants at Different Temperatures

Designation	**Thermodynamic Parameters at Different Temperatures (K)**								**ΔS_{mic} kJ mol $^{-1}$K^{-1}**
	293		303		313		323		
	- ΔG_{mic}	**ΔH_{mic}**	**- ΔG_{mic}**	**ΔH_{mic}**	**-ΔG_{mic}**	**ΔH_{mic}**	**-ΔG_{mic}**	**ΔH_{mic}**	
MPA-PEG600	19.5	39.1	21.9	38.7	24.5	38.1	27.2	37.4	0.20
MPA-PEG1000	20.2	67.7	24.2	66.7	27.1	66.8	29.6	67.3	0.30
MPA-PEG2000	23.4	52.78	25.9	52.88	28.7	52.68	31.5	52.48	0.26
APA-PEG600	12.68	45.92	14.8	45.8	17.2	45.2	19.6	45	0.20
APA-PEG1000	21.9	51.35	24.4	51.35	27.15	51.1	29.6	51.15	0.25
APA-PEG2000	16.5	50.89	18.9	50.79	21.4	50.59	23.9	50.39	0.23

Table (3.7): Thermodynamic Parameters of Micellization for RFA-PEG and RFAP-PEG Surfactants at Different Temperatures

Designation	**Thermodynamic Parameters at Different Temperatures (K)**								ΔS_{mic} kJ mol $^{-1}$K^{-1}
	293		303		313		323		
	$-\Delta G_{mic}$	ΔH_{mic}	$-\Delta G_{mic}$	ΔH_{mic}	$-\Delta G_{mic}$	ΔH_{mic}	$-\Delta G_{mic}$	ΔH_{mic}	
RFA-PEG600	14.38	53.01	16.69	53	19.06	52.93	21.5	52.7	0.23
RFA-PEG1000	17.07	56.18	19.4	56.35	21.6	56.65	24	56.7	0.25
RFA-PEG2000	21.7	42.76	24.2	42.46	26.8	42.06	29.6	41.46	0.27
RFA-PEG1000-ST	17.3	41.3	19.6	41	22.19	40.41	24.7	39.9	0.2
RFA-PEG2000-ST	21.7	51.5	24.2	51.5	26.8	51.45	29.6	51.15	0.25
RFAP-PEG2000	19.9	50.42	22.4	50.32	25.06	50.06	27.7	49.82	0.24
RFAP-PEG2000-ST	24.4	34.2	25	35.6	25.3	37.3	28	36.6	0.2

*** $-\Delta G_{mic}$ and ΔH_{mic} in kJ mol^{-1}**

This can be attributed to that the increased molecular weight of PEG leads to formation of numerous hydrogen bonds between water and PEG, which introduces some restriction on motion of surfactants. The dissolution of the oxyethylene units has been stated **[Riess et al (1958) and Hudson & Pethica (1967)]** to be the major contributing factor to the positive entropy of micellization in polyoxyethylenated nonionics. This explanation is consistent with the re-evaluation of the concept **[Wertz (1980)]** of entropy of solution.

The listed values of ΔH_{mic} are all positive, in contrast to those of Crook and coworkers **[Crook (1964)]**, who reported negative ΔH_{mic} values at 298K for p-tert-octylphenoxypoly(ethylenoxy ethanol)s containing less than four oxyethylene units. By increasing the number of oxyethylene units in the molecule the values of ΔH_{mic} increase. This is in accord with the observations of other investigators **[Riess et al. (1958) and Hudson & Pethica (1967)]**, indicating that a greater number of hydrogen bonds between polyoxyethylene chain oxygen and water molecules is broken in the micellization process as the number of oxyethylene units in the molecule increases.

3.3.2. Thermodynamic Parameters of Adsorption

The values of ΔG_{ad}, ΔH_{ad} and ΔS_{ad} for nonionic surfactants are calculated and listed in ***Tables (3.8&3.9).*** All ΔG_{ad} values are more negative than ΔG_{mic}, indicating that adsorption at the interface is associated with a decrease in the free energy of the system. This may be attributed to the effect of steric factor on inhibition of micellization more than its effect on adsorption. It is apparent that the work of transfer, which measures the ease of adsorption to form a monolayer at zero surface pressure relative to ease of micellization, shows appreciable change with temperature, but increases with increase in the number of oxyethylene units in the molecule. The values of ΔS_{ad} are all positive and have greater values than ΔS_{mic} for the prepared nonionic surfactants. This may reflect the greater freedom of motion of the hydrophobic chains at the planar air-aqueous solution interface compared to that in the relatively cramped interior beneath of the convex surface of the micelle. On the other hand, the positive values of ΔH_{ad} are much greater, in case of the prepared nonionic surfactants, than the corresponding values of ΔH_{mic}. This phenomenon becomes less pronounced with increasing the molecular weight of PEG. This also indicates that the micellization becomes favorable with increasing the molecular weight of PEG molecules. The negative values of ΔH_{ad} indicate that more bonds between polyoxyethylene chain oxygen and water molecules are broken in the process of adsorption at the air aqueous solution interface than in micellization **[Hirato et al.(1991)].**

In general, it is obvious that the increase in the size of the hydrophilic group in the synthesized non-ionic surfactants based on rosin surfactants inhibits micellization more than adsorption at the air-aqueous solution interface. On the other hand, it was observed that APA-PEG surfactant have more negative values of ΔG_{ad} than that based on MPA-PEG surfactants. This may be explained by that the surfactants based on APA-PEG favor the adsorption at interface than that based on MPA-PEG surfactants. The values of ΔS_{ad} are all positive and have greater values than ΔS_{mic} for nonionic surfactants. On the other hand, the positive values of ΔH_{ad} are much lower than the corresponding values of ΔH_{mic}. This indicates that the dehydration -breaking of hydrogen bonds- at adsorption is easier than at micellization.

Table (3.8): Thermodynamic Parameters of Adsorption for Rosin Adducts Surfactants at Different Temperatures.

Designation	Thermodynamic Parameters at Different Temperatures (K)								ΔS_{ad} kJ $mol^{-1}K^{-1}$
	293		303		313		323		
	$-\Delta G_{ad}$	ΔH_{ad}	$-\Delta G_{ad}$	ΔH_{ad}	$-\Delta G_{ad}$	ΔH_{ad}	$-\Delta G_{ad}$	ΔH_{ad}	
MPA-PEG600	23.77	43.6	26.28	43.4	29.10	42.8	32.04	42.25	0.23
MPA-PEG1000	24.4	45.8	29.5	43.18	32.01	43.10	33.5	43.99	0.34
MPA-PEG2000	26.9	43.4	29	43.6	31.7	34.37	34.6	42.9031	0.35
APA-PEG600	15.3	55	17.9	54.9	21.8	53.2	24.5	53	0.30
APA-PEG1000	26.5	90.6	28.7	92.4	31.4	92.9	35	94.1	0.40
APA-PEG2000	22.3	50 86	27.9	48.09	25.8	52.36	30.062	50.68	0.43

*** $-\Delta G_{ad}$ and ΔH_{ad} in kJ mol^{-1}**

Table (3.9): Thermodynamic Parameters of Adsorption for RFA and RFAP Surfactants at Different Temperatures

Designation	Thermodynamic Parameters at Different Temperatures (K)								ΔS_{ad} kJ $mol^{-1}K^{-1}$
	293		303		313		323		
	$-\Delta G_{ad}$	ΔH_{ad}	$-\Delta G_{ad}$	ΔH_{ad}	$-\Delta G_{ad}$	ΔH_{ad}	$-\Delta G_{ad}$	ΔH_{ad}	
RFA-PEG600	17	79.66	19.5	80.4	22.3	80.32	26.4	80.1	0.33
RFA-PEG1000	21.3	60.8	23.4	61.3	25.4	62.2	28.9	61.5	0.28
RFA-PEG2000	25.6	62.3	28.06	62.9	31.6	62.3	35.4	61.7	0.3
RFA-PEG1000-ST	18.7	60.41	20.9	60.91	23.7	60.81	26.3	60.91	0.27
RFA-PEG2000-ST	27.25	48.7	30.22	48.48	32.8	48.1	35.1	48.38	0.26
RFAP-PEG2000	19.9	44.5	22.1	44.56	25.06	43.8	27.7	43.36	0.22
RFAP-PEG2000-ST	24.1	22.48	22	25.8	25.3	24.7	28	23.6	0.16

*** $-\Delta$Gad and ΔHad in kJ mol-^{1}**

3.4. EVALUATION OF THE PREPARED SURFACTANTS AS OIL SPILL DISPERSANT

Dispersion of a liquid phase into another relatively immiscible phase frequently occurs in operations involving liquid-liquid contacting. Some of these dispersions are desirable, as in the food and cosmetic industry, while there are many situations where such dispersions, or emulsions, are undesirable as in the petroleum industry. The well use of dispersants generally is preferred over the other options if there is insufficient time for prior mechanical recovery of the oil. If use of dispersants will prevent environmental damage, dispersion of the spilled oil should be strongly considered. Also, if dispersion of oil can reduce or eliminate hazardous conditions, use of dispersants is recommended.

The theory behind the use of dispersants in oil incidents is that they provide a mean of accelerating the rate of natural degradation of oil. Increasing the surface area of the oil by dispersion is thought to accelerate the biological degradation of the spilled oil. The use of chemical dispersants as a counter measure to accidental oil spills at sea is now a technique accepted worldwide. In recent years, the commercial availability of dispersants, containing less toxic chemicals and more efficient surfactants, has renewed interest for basic studies on dispersant effectiveness and on the fate of dispersed oil in the marine environment. The surface activity of dispersants is of great importance in a wide variety of industrial and technological operations involving foam, froth formation, dispersion and emulsification and in determining biological activity. The role of solvents in effectiveness of dispersants is of primary importance. The solvents enable the active agent or surfactant to mix with and penetrate into the oil slick and thus form the emulsion. The solvent usually comprises the bulk of the dispersant product and may range from petroleum solvents, such as kerosene, to water solvents. Petroleum-based solvents not only represent the most toxic component in the dispersant product but also dissipate most rapidly in the water environment. To reduce toxicity, non-aromatic hydrocarbons water-miscible solvents (ethylene glycol ethers) have been used in more recent dispersant formulations. The exact details of dispersant formulations are proprietary, but the chemical characteristics of these formulations are broadly known **[Broch et al.(1987) and Wells & Mackay (1985)]**.

The correct understanding of the relationships between chemical structure and properties of surfactants is important to both their effective use and to design of new surfactants. Some reliable information is available on various structural effects in ionic surfactants. On the other hand, only a limited amount of reliable information is available for nonionics with much of the data in the literature being insufficient both in reliability and in the variety of structures dealt with, mainly because of the difficulty in obtaining well-characterized compounds.

The following section pertains to:

- Test the capability of the prepared polymeric compounds in reducing the oil / water interfacial tension (IFT),
- Study the effect of molecular weight of the hydrophilic moiety and the hydrophile-lipophile balance (HLB) of the prepared polymeric compounds on their dispersion potency,
- Evaluate the prepared surfactants as oil spill dispersants (OSD)

In this respect, asphaltenic crude oil, paraffinic crude oil and seawater were used to evaluate the dispersion efficiency of the prepared surfactants.

3.4.1 Dispersion Capability of the Prepared Surfactants as OSD

Dispersants effectiveness is defined as the amount of oil that the dispersants puts into the water column versus that which remains on the surface. There are many factors that influence dispersant effectiveness: sea energy, oil composition, state of oil weathering, rate of dispersants application, dispersant type, temperature, salinity of the water, etc. The most important factor for dispersants effectiveness is the composition of the oil, followed very closely by sea energy and amount of dispersant applied. Effectiveness of dispersants is relatively easy to measure in the laboratory; however there are many nuances in testing procedures. Once, concern is that these tests are representative of real conditions. Since it is impossible to mimic all conditions directly, it is necessary to consider the important factors such as sea energy and salinity while considering the laboratory tests as a form of screening or representative value, rather than a direct representation of what can be obtained in the field.

"Field measurements" of the dispersant effectiveness are also fraught with difficulty because it is very difficult to measure the concentration of oil in the water column over wide distances in appreciably small times. Because there are no commonly available oil slick thickness measurements with which to assess the amount of oil remaining on the surface and because of the fact that the sub-surface oil often moves differently than the surface slick. Any field measurement at this time is best viewed as an estimate.

The effectiveness is indicated by the presence of coffee-colored dispersed-oil plume in the water column. This is visible form ships and aircraft. Lack of the coffee-colored plume indicates no or very little effectiveness.

The dispersion capability of individual non-ionic surfactants (MPA-PEG, APA-PEG, RFA-PEG, RFA-PEG-ST, RFAP-PEG and RFAP-PEG-ST) was tested on both asphaltenic(Bakr) and waxy(Qarun) crude oils. The test was carried out on surfactants to oil ratio (SOR) ranging from 1:1 to 1:100. The relation between SOR and dispersion efficiency for all the prepared surfactants are represented in ***Figures (3.13) and (3.14).*** Furthermore, the data of dispersion efficiency is supplied here in ***Tables (3.10) & (3.11).***

The data of WSL method was provided from UV spectroscopy. A calibration curve (based on Beer's low), which represents the variation of asphaltene absorbance versus its concentration was drawn. The relation between absorbance values of Bakr and Qarun crude oils versus their concentrations were determined and plotted in ***Figure (3.15)***. These data were fitted to the equation; Y= a + bx where; Y represents the absorbance and X is the concentration of the asphaltene. The following equations (with $r^2=0.9997$) were obtained:

Absorbance(Bakr Crude) = 0.0013 + 0.1964 C (3.8)
Absorbance(Qarun Crude Oil)= 0.0008+ 0.142C (3.9)

The equations were reused to derive the concentration of crude oil from the measured absorbance values. The data obtained confirms that the results of screen tests were in good agreement with WSL and proves the validity of our quick comparative tests. It is obvious that nonionic surfactants based on MPA-PEG have high dispersion capabilities than those based on APA-PEG for both wax and asphaltenic crude. It was also observed that the prepared RFA-PEG surfactants have high dispersion efficiencies for wax crude oil (Qarun crude oil) than other nonionic surfactants. The data reveal that MPA-PEG600 and RFA-PEG600 have the maximum efficiency (90-80 %) at SOR 1:5.

These results can be correlated with the thermodynamic parameters of micellization and adsorption. It was previously found that the prepared surfactants favor adsorption than micellization. The data of dispersion capabilities of the prepared surfactants can be also correlated with HLB values of these surfactants. It was aforementioned that the prepared surfactants have various solubilities in water and diverse actions towards oil and water. It is well known that the surfactant having HLB between 1 and 8 promotes the formation of water- in-oil emulsions and one with an HLB between 12 and 20 promotes the formation of oil-in-water emulsions **[Becher(1977)].** A surfactant having HLB between 8 and 12 may promote either type of dispersants. In the present study, it was observed that the surfactants have HLB (12-16) show good dispersion efficiencies. This behavior reflects the dependence of the dispersion power on the presence of surfactant molecules in the soluble form rather than micelles **[Rosen (1978)].** This can be attributed to the solubilization of crude oil into the hydrophobic interior core of micelle **[Fujimoto (1985)].** The high dispersion power of surfactants based on PEG 2000 at low SOR reflects the hydration of long hydrophilic groups into bulk phase which prevents the crude oil to penetrate the exterior region of micelle to arrive to their interior core and solubilize there, this was in accordance with Rosin's findings **[Rosen(1978)].**

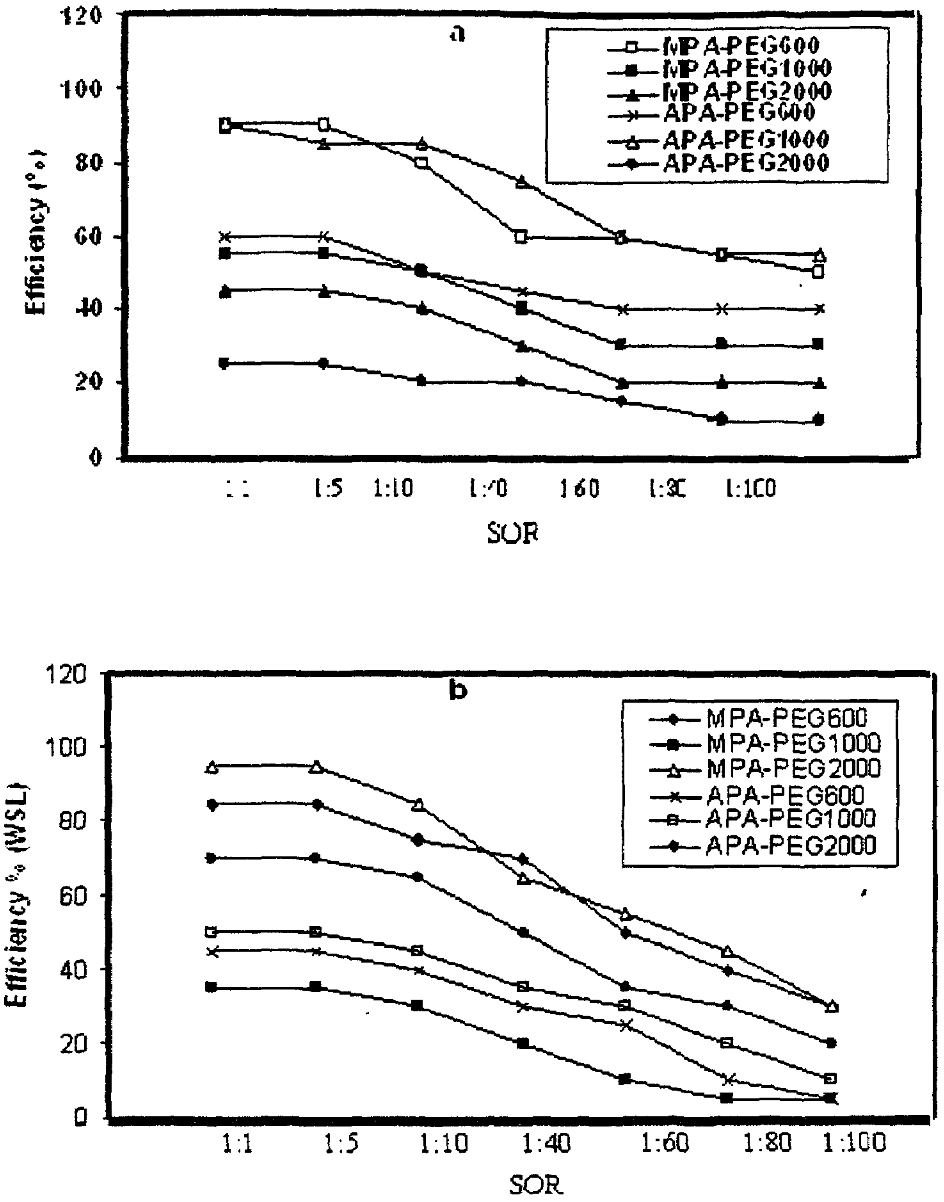


Figure (3.13): The relation between SOR and dispersion efficiency for MPA and APA surfactants for a-Asp, b-wax

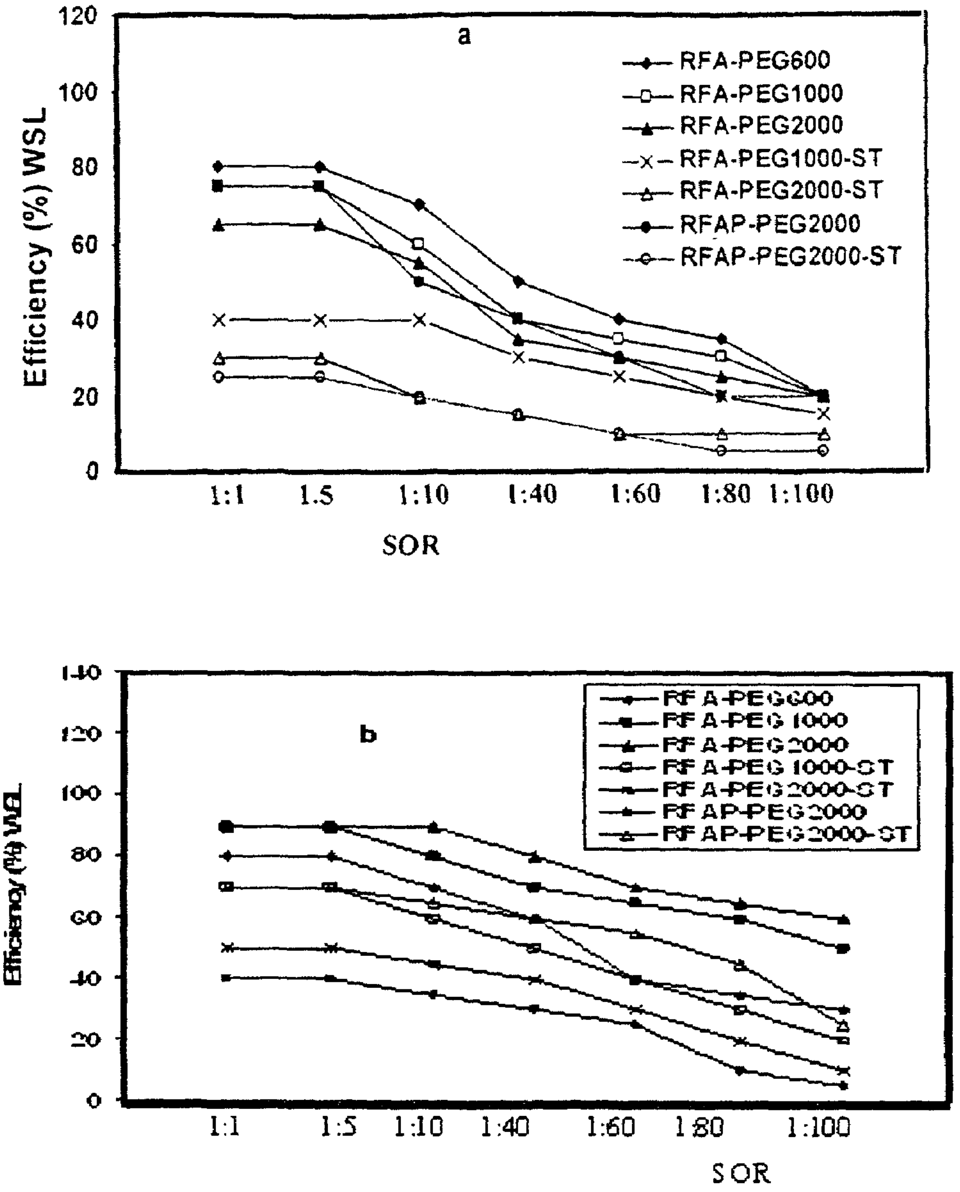


Figure (3.14): The relation between SOR and dispersion efficiency for rosin RFA&RFAP for a-Asph. crude, b-wax crude

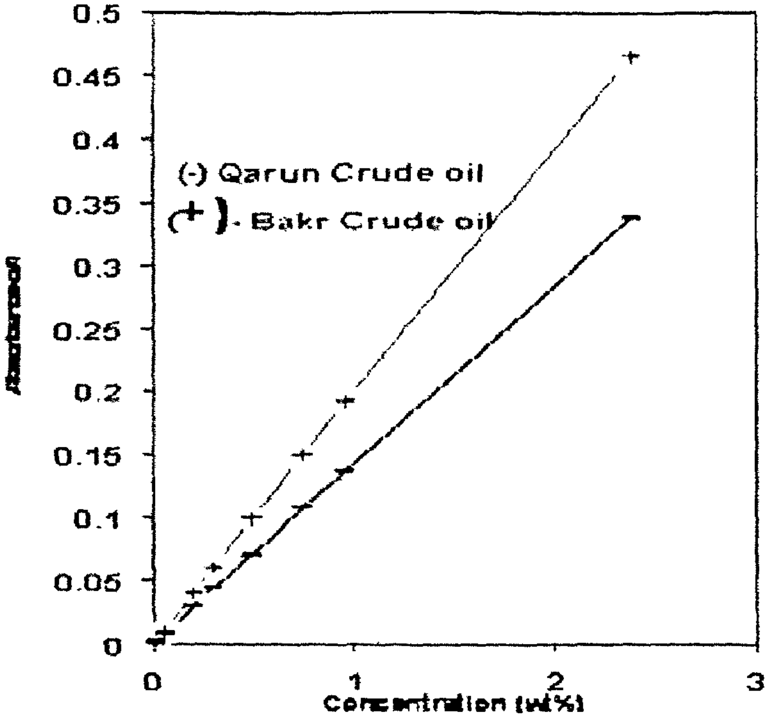


Figure (3.15) The relation between absorbance values of Bakr and Qarun crude oils versus their concentrations

Table (3.10): IFT, Screen test and WSL for Surfactants Based on MPA and APA surfactants with asphaltenic and waxy crude oils

Designation	*HLB*	*SOR**	*IFT with sea water (mNm^{-1})*	*Dispersion Efficiency (screen test)*		*Efficiency Index (EI)*	
				Bakr	*Qarun*	*Bakr*	*Qarun*
MPA-PEG600	16.7	1:5	0.0169	A	A	90	85
MPA-PEG1000	17.9	1:5	1.4	C	D	55	35
MPA-PEG2000	18.3	1:1	1.7	D	A	45	95
APA-PEG600	15.8	1:5	0.33	C	D	60	40
APA-PEG1000	17.3	1:10	0.077	B	D	85	50
APA-PEG2000	18.1	1:1	3.9	E	B	25	70

SOR*: *Surfactant Oil Ratio* (*Surfactant dissolved in water*,40%).

A: Very good dispersability.
B: Good dispersability.
C: Moderate dispersability.
D: Bad dispersability.
E: Very bad dispersability.

Table (3.11): IFT, Screen test and WSL for Surfactants Based on RFA and RFAP surfactants with asphaltenic and waxy crude oils

Designation	*HLB*	*SOR**	*IFT with sea water (mNm^{-1})*	*Dispersion Efficiency (screen test)*		*Efficiency Index (EI)*	
				Bakr	*Qarun*	*Bakr*	*Qarun*
RFA-PEG600	12.2	1:5	0.0925	B	B	80	80
RFA-PEG1000	14.4	1:5	0.0953	B	A	75	90
RFA-PEG2000	16.7	1:5	0.153	C	A	65	90
RFA-PEG1000-ST	12.1	1:5	2.32	D	B	40	70
RFA-PEG2000-ST	15	1:1	3.15	D	C	30	50
RFAP-PEG2000	13	1:10	1.13	B	D	75	40
RFAP-PEG2000-ST	11	1:1	4.52	E	B	25	70

SOR*: Surfactant Oil Ratio (Surfactant dissolved in water,40%).
A: Very good dispersability.
B: Good dispersability. **D: Bad dispersability.**
C: Moderate dispersability. **E: Very bad dispersability.**

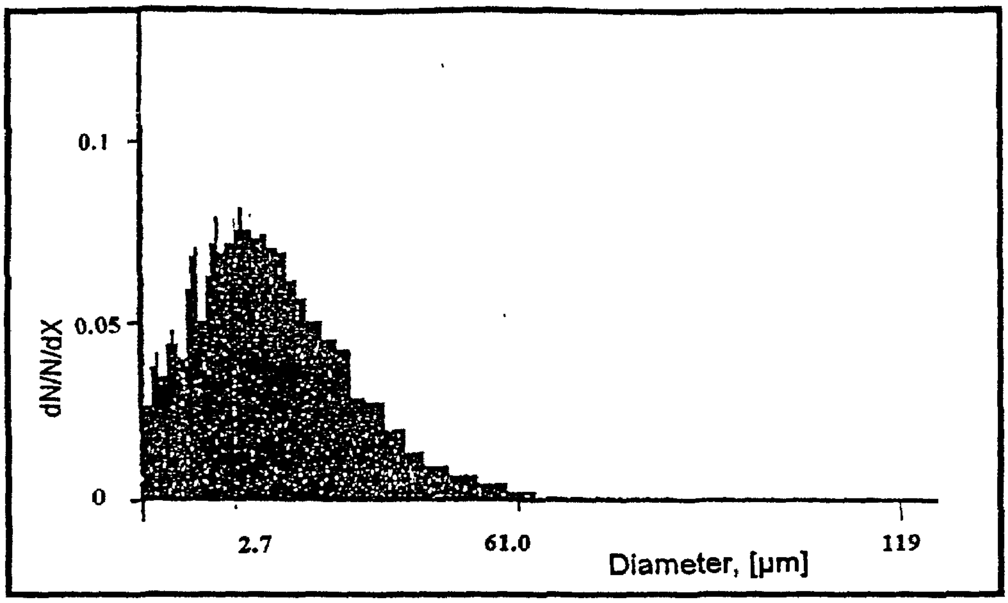
At the same time, the long hydrophilic chain reduces the hydrophobicity of the surfactant molecule; hence, the solubilization efficiency is reduced **[Cowell et al. (2000)].** This behavior can be correlated with the ability of surfactants to reduce surface tension at CMC (γ_{CMC}), ***Tables (3.3) & (3.4).*** Careful inspection to the data listed in these tables, one can observe that the ability of surfactants based on PEG 600 and 1000 to reduce γ_{CMC} is much greater than that for those based on PEG 2000. This reduction facilitates the dispersion of oil into fine droplets **[Rosen(1978)]**. From the pervious results, it can be concluded that surfactants based on PEG 600 and 1000 have better dispersion efficiency than nonionic surfactants that based on PEG 2000. This is in agreement with the result given by Broch et.al. [**Broch et al. (1987)**]. They deduce that better dispersions are referred to the solubility and structure of hydrophilic groups.

It was believed that dispersants created smaller droplets, which were obviously more stable in the water column **[Clayton et al.(1993)].** For this respect, the droplet size and their distribution can be measured from particle size technique. In the present system, the particle size and dispersion distribution of prepared surfactants with crude oil were measured at different concentrations of surfactants.

A typical distribution of droplet sizes for Bakr crude oil without and with the use of RFA-PEG600 dispersant is shown in ***Figure (3.16) and (3.17) Figure (3.16)*** demonestrates that the particles of crude oil without surfactants are widely distributed at different particle size diameters. Whereas ***Figure (3.17)***shows that the particle size distribution of crude oil in presence of dispersants was accumulated together at low particle size and at narrow range regardless the surfactant concentration. Several researches found that droplet sizes did not change with the amount of dispersion used, but that more dispersant simply created a larger amount of droplets of relatively the same size. **[Clayton et al. (1993), Fingas et al. (1995) and Lunel (1995)].** Furthermore, the data reveals that the dispersion efficiency was affected by molecular weight of PEG. It was observed that the dispersion efficiency of PEG 2000 versus asphaltenic crude oil (Bakr) was decreased. This may be due to that the increase of ethylene oxide number leads to coil the molecule and hinder the adsorption on the interface further dispersion.

It can also be shown that there is an inverse correlation between IFT and SOR as tabulated in ***Tables (3.10) and (3.11)***. These results are in good agreement with basic principles of emulsion formation **[Boyd et al. (1972) and Mukherjee et al.(1983).** The surfactants with appropriate HLB i.e. 13-16 in the case of crude oil, will concentrate at the o/w interface. The decreasing of IFT, facilitates the deformation of the interface and hence the disruption of droplets in to yet smaller droplets.

Furthermore, surfactant molecules also form a continuous film which stabilizes the new interface and prevents the coalesence. The most effective nonionic surfactants appear to be those with an HLB around 10, having at the same time long hydrophobic chains and long polyoxyethylene chains. Under these conditions, the interfacial tension is generally quite low and the surface viscosity is relatively high since these long chains add rigidity to the interface, making it more gel – like **[Boyd et al. (1972)]**.



Figure(3.16): Droplet size Distribution of Crude oil without dispersants

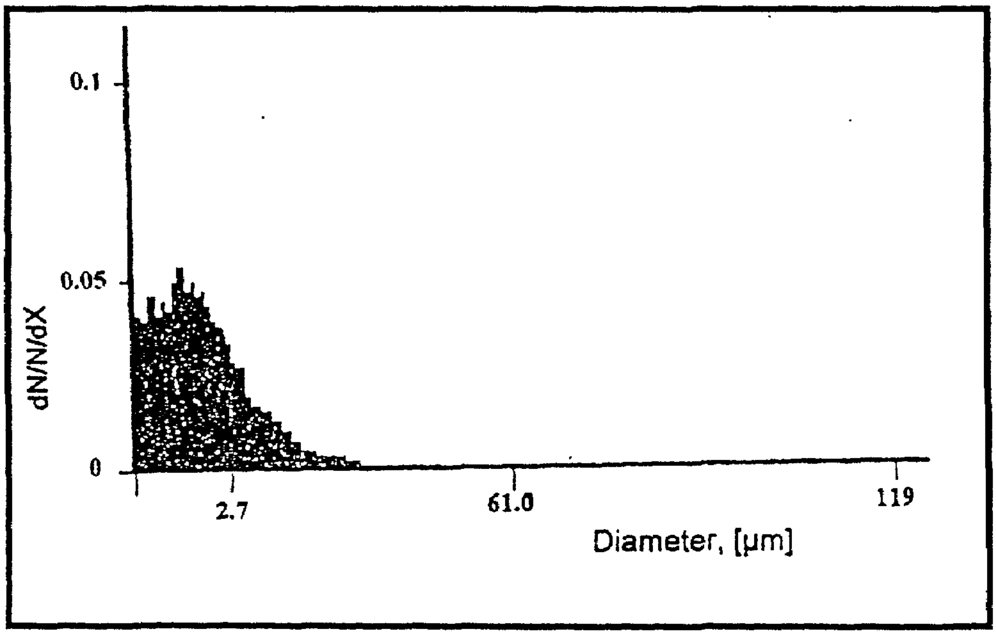


Figure (3.17): Droplet size distribution of treated crude oil with RFA-PEG600 dispersant

The previous data indicate that the surfactants based on PEG600 which have better solubility in crude are of good dispersion efficiency for both asphaltenic and wax crude oil. It was observed that the surfactants based on PEG2000 and contain ST show good dispersion efficiency in wax crude. This can be attributed to good solubility of these surfactants in wax crude oil which contain linear paraffin that can matched with ST and PEG2000.

The obtained data for the individual surfactants as dispersants are not enough to accept the individual molecule as oil spill dispersant. So that,most commonly used dispersants are formulated from more than one surfactants to enhance the dispersion capability.

3.4.2. Dispersion Capability of Blends of Rosin Surfactants

Many surfactant mixtures for treating oil spills have been promoted in the last two decades to overcome the extensive problems and costs of physical recovery. All of these formulations contain surfactants as active ingredients. Dispersants in particular, promise to reduce the efforts and costs of cleaning up oil spills. A typical dispersant formulation consists of a pair of non-ionic surfactants in proportions to yield an average HLB of 10. Studies have been done on this mixture [**Brandvik & Daling(1990) and Exxon Research Engineering(1997)**]. Hydrophilic-lipophilic balance, HLB and the chemical structure of the surfactants exert a large influence on the rate of coalescence of emulsions containing blends of non-ionic surfactants. The best stability was obtained by mixing surfactants varied in HLB values [**Boyd et al. (1972), and Nael & El-Sabagh (1997)**].

In order to estimate the validity of this observation with asphaltenic and waxy crude oil dispersions, blends of the prepared nonionic surfactants were prepared. It is apparent that both HLB and chemical constitution of the dispersants exert a large influence on the percentage of dispersion. MPA-PEG600(HLB=16.7), RFA-PEG600 (HLB=12.2) and APA-PEG1000 (HLB=17.3) (nonionic) were selected as blend for asphaltenic crude oil. MPA-PEG600 (HLB= 16.7), RFA-PEG600 (HLB=12.2) and RFA-PEG1000 (HLB=14.4) were used to prepare blend to apply as oil spill dispersants for petroleum waxy crude such as Qarun as explained in the experimental section. On the other hand, a third surfactant was added, in some cases, to form ternary surfactant systems. In all cases the surfactant were blended in different weight %. HLB values of the surfactant blends were calculated as, HLB blends= HLBa Xa + HLBb Xb + HLBc Xc, where X is mole fraction of surfactant a,b and c. In this respect, dispersant 1 (MPA-PEG600, RFA-PEG600 and APA-PEG1000) was used to prepare blends having different HLB values varied from 12.2to 17.3. Dispersant 2 (MPA-PEG600, RFA-PEG600 and RFA-PEG1000) was selected in order to study the effect of SOR on dispersion efficiency and interfacial tension reduction (IFT) between oil and water. The composition of the blends, their designation and HLB values were recorded in ***Table (3.12)*** for the prepred surfactant blends. It can be seen that increasing the number of EO units in the molecule leads to an appreciable increase in the HLB values of blends. The data of WSL efficiency of blends at different SOR were determined and listed in ***Tables (3.13&3.14)***. The relations between HLB of blends and their IFT values were represented in ***Figure (3.18)***.

As mentioned before, the oil-water interfacial tension (IFT) falls as the surfactant concentration increases and then attains a constant value at and above the concentration where surfactant aggregation occurs (CMC). The aggregation may occur either in the oil phase or in the aqueous phase, depending on conditions. This work will concern the dependence of IFT on the chain length of the hydrophobic moiety of the surfactant molecule and upon the PEG units in the hydrophilic moiety. It is known thatminimum IFT results for the condition where phase inversion occurs[**Aveyard et al. (1986)**], i.e. where the coarse emulsion formed by agitation of the oil and aqueous phases changes from an oil - in - water (O/W) emulsion to a water -in-oil (W/O) emulsion, or vice versa. In case where an O/W emulsion is given, surfactant is found to reside mainly in the aqueous phase, which is a swollen miceller solution (or O/W microemulsion).

Table (3.12): HLB Values of Dispersant 1 and Dispersant 2

HLB	Dispersant blends 1			Dispersant blends 2		
	X* MPA-PEG600 HLB=16.7	X* RFA-PEG600 HLB=12.2	X* APA-PEG1000 HLB=17.3	X* MPA-PEG600 HLB=16.7	X* RFA-PEG600 HLB=12.2	X* RFA-PEG1000 HLB=14.4
12.5	0.08	0.9	0.02	0.05	0.85	0.1
12.8	0.05	0.87	0.08	0.05	0.8	0.15
13	0.15	0.8	0.05	0.15	0.75	0.1
13.2	0.1	0.8	0.1	0.15	0.7	0.15
13.4	0.2	0.75	0.05	0.15	0.65	0.2
13.6	0.15	0.7	0.15	0.15	0.6	0.25
13.8	0.1	0.65	0.25	0.15	0.55	0.3
14	0.25	0.6	0.15	0.28	0.5	0.22
14.2	0.2	0.6	0.2	0.3	0.45	0.25
14.5	0.25	0.5	0.25	0.4	0.4	0.2

*** X = Mole fraction of the indvidual surfactant in the blend**

Table (3.13): IFT, Screen Test and WSL for the Blend 1 with Bakr Crude Oil

HLB	**SOR**	**Interfacial tension, IFT, with sea water,mNm^{-1}**	**Dispersion Efficiency (screen test)**	**Efficiency index (EI)**
14.5	1:50	0.09	D	36
	1:25	0.08	D	48
	1:20	0.02	C	61
	1:10	0.009	C	70
	1:5	0.005	B	87
13.5	1:50	0.008	B	86
	1:25	0.008	B	88
	1:20	0.005	B	90
	1:10	0.001	A	92
	1:5	0.0007	A	94
13	1:50	0.007	B	88
	1:25	0.004	B	90
	1:20	0.0008	A	92
	1:10	0.0006	A	93
	1:5	0.0004	A	95
12.5	1:50	0.09	D	40
	1:25	0.08	C	55
	1:20	0.04	C	68
	1:10	0.006	B	75
	1:5	0.004	B	81

Table(3.14): IFT,Screen Test and WSL for the Blend 2 with Qarun crude oil

HLB	SOR	Interfacial Tension, IFT, with sea water,mNm^{-1}	Dispersion Efficiency (screen test)	Efficiency index (EI)
12.5	1:50	0.08	D	45
	1:25	0.05	C	60
	1:20	0.03	C	70
	1:10	0.006	B	84
	1:5	0.007	B	86
13	1:50	0.07	C	70
	1:25	0.009	B	85
	1:20	0.007	B	86
	1:10	0.006	B	88
	1:5	0.004	A	91
13.5	1:50	0.009	B	85
	1:25	0.009	B	87
	1:20	0.008	B	90
	1:10	0.0005	A	92
	1:5	0.0004	A	94
14	1:50	0.008	B	88
	1:25	0.004	B	90
	1:20	0.0007	A	92
	1:10	0.0003	A	93
	1:5	0.0001	A	95

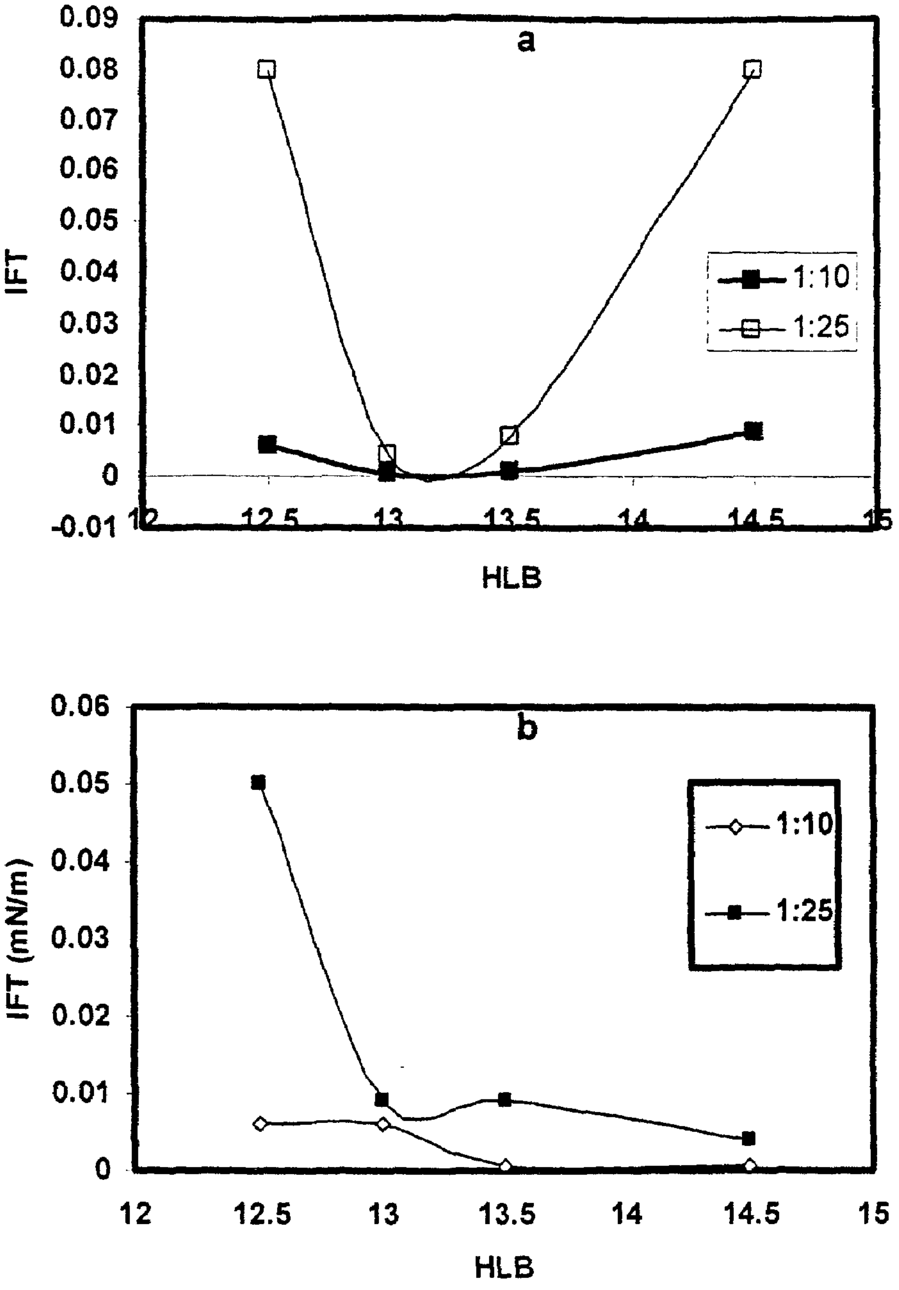


Figure (3.18): Relation Between HLB of Blends and IFT Values for a)Bakr and b)Qarun crude oils

At the equilibrium in water-oil emulsions, all of the aggregated surfactant is present in the oil and it forms W/O microemulsion. The way in which the shape, size and curvature of the surfactant aggregates change as phase – inversion conditions are approached has been discussed in some detailed in terms of surfactant molecular geometry by Mitchell and Ninham **[Mitchell& Ninham(1981)]** and in terms of a statistical mechanical model by Mukherjee et al. **[Mukherjee et al.(1983)].**

It has been proposed in this work to study the changes in IFT with respect to the PEG units and the methylene groups in the hydrophilic and hydrophobic portions in the surfactant molecule. Under these conditions the interfacial tension is generally quite low and the surface viscosity is high since these long chains add rigidity to the interface and making it more gel like **[Boyd et al. (1972)].** The lowering of IFT and the improved stability of O/W emulsions combining surfactants with high and low HLB have been explained through some specific molecular association of surfactants at the interfaces **[Boyd et al.(1972) and Takamura et al.(1979)].** It was also observed that the lower IFT values were determined for dispersant 1 (which has HLB=13) at SOR 1:20 . This may give indirect evidence that the HLB and interfacial tension are linked in the same way by the dispersion capability. It is obvious that the interfacial tension of the mixed surfactants is less than of individual surfactant. On the other hand, increasing the dispersion capability could be attributed to the intermolecular interaction between the two polymeric molecules **[Tenhu & Sundholm (1992/1993) and Abdel-Azim et al.(1995)]**. Furthermore, it is clear that the relation between dispersant mixing ratio and the efficiency index at DOR 1:25 and 1:10 (regarding to environmental regulations). The most effective nonionic surfactant blend appears to be good with an HLB 12.5 to 13.5, having long hydrophobic chains and long polyoxyethylene chains. This mean that the HLB concept plays an important role in the dispersion capability of dispersant blend. The relation between HLB of surfactant blendsand their effeciencywith Bakr and Qarun crude oils in ***Figure (3.19)***.

It is also obvious that the asphaltenic Bakr crude achieve good results with dispersants having HLB=12.5-13. This finding may be explained on the bases of the following speculations:

1. The decrease in the HLB value increases the solubility of the surfactant in the oil phase (dispersed phase). When the dispersant is initially introduced to the oil-in-water

emulsion, it will be thermodynamically stable at the interface of the oil droplets for asphaltenic Bakr crude oil. Accordingly, the surfactants possessing low HLB migrate faster to the interface than those having high HLB. As a result of such enhanced migration toward the interface, the surfactant forms a continuous hydrophobic pathway between the dispersed oil droplets. This leads to a stabilization of the interfacial water film surrounding the oil droplets.

2. Another point of view regarding the enhanced dispersion efficiency of wax crude oil with the more hydrophilic surfactants is based on the stability of emulsions containing wax. The higher HLB surfactants reveal higher dispersion efficiency.

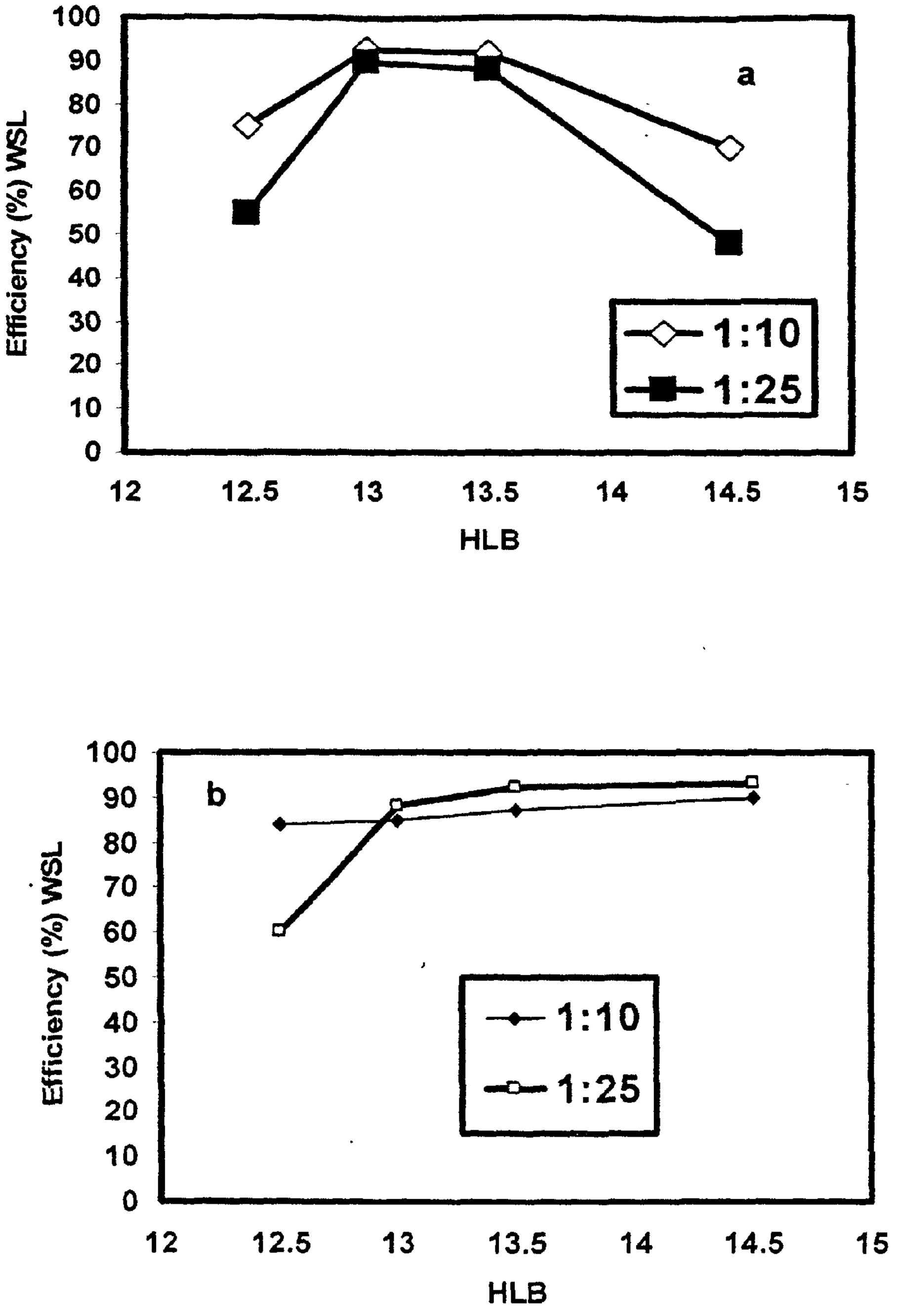


Figure (3.19): Relation beween HLB of Surfactant Blends and their Efficiency with a)Bakr and b)Qarun crude oils

These behaviors reflect the dependence of the dispersion power on the presence of surfactant molecules in the soluble form rather than micelles **[Adal et al. (1994)]**. This can be attributed to the solubilization of crude oil into the hydrophobic interior core of micelle **[Naylar (1986)]**.

A real improvement in the percentage of dispersed oil was observed for the blends when compared to the individual *MPA-PEG600* performance. The interactions between components of dispersant 1 are favorable for interface stabilization and give a quite good dispersion test. Finally, The lowering of IFT and the improved stability of O/W emulsions combining surfactants with high and low HLB have been explained through some specific molecular association of surfactants at the interfaces **[Takamura et al. (1979) and Tenhu et al. (1992/1993)]**.