RESULTS&DISCUSSION

III- RESULTS AND DISCUSSION

Qarun field is located in the Egyptian western desert and as almost of the producing fields in western desert, Qarun field produces a paraffinic crude with a relatively high pour point but the paraffinic chains are completely different. Qarun crude is produced by Qarun Petroleum Co (QPC). The producing wells are around 9700 feet deep with bottom hole temperature of 216 °F (102 °C). There are different types of Qarun crude oils such as Bensuif (BS), Karama, Wady El-Rayan crude oils. These crude oils have different pour points ranged from 39 to –3 °C. The early production started on Nov. 1995 from 2 wells with an average daily rate of 3500-barrel oils per day (BOPD) increased to 10,000 BOPD from 6 wells using rental production facilities of test heaters and separators **[123].** The crude oil is being trucked to El-Tebbin storage tanks and then pumped to Mostoroud refinery. During this period (early production phase) the agreement with the PPC was to ship QPC crude with (9 °C) pour point and if the pour point exceeds this temperature, QPC has to pay for the heating costs (using steam) for El-Tebbin tank bottoms. After that, QPC work to pump the crude for loading Dahshour area through 16" pipe line with a total length of 49.5 Km from Qarun base to Dahshour storage tanks. Bottomless efforts have been done during the early production phase in order to find a pour point depressant chemical suitable to achieve the target pour point

and to be within the Western desert crude oil pour point shipping specifications. There are three types of crude oils were produced which designated as Karama, BeniSuif (BS) and Qarun mix crude oils. Their physicochemical characteristics and pour points were represented in experimental section. The currently used commercial additives success to decrease pour point of BS and Karama to 21 and 12 °C at additive concentration 2000 ppm, respectively.

The present work aims to evaluate the efficiency of some rosin acid derivative surfactants as pour point depressants for mixed base crude oil.

3.1 QARUN CRUDE OIL COMPOSITION:

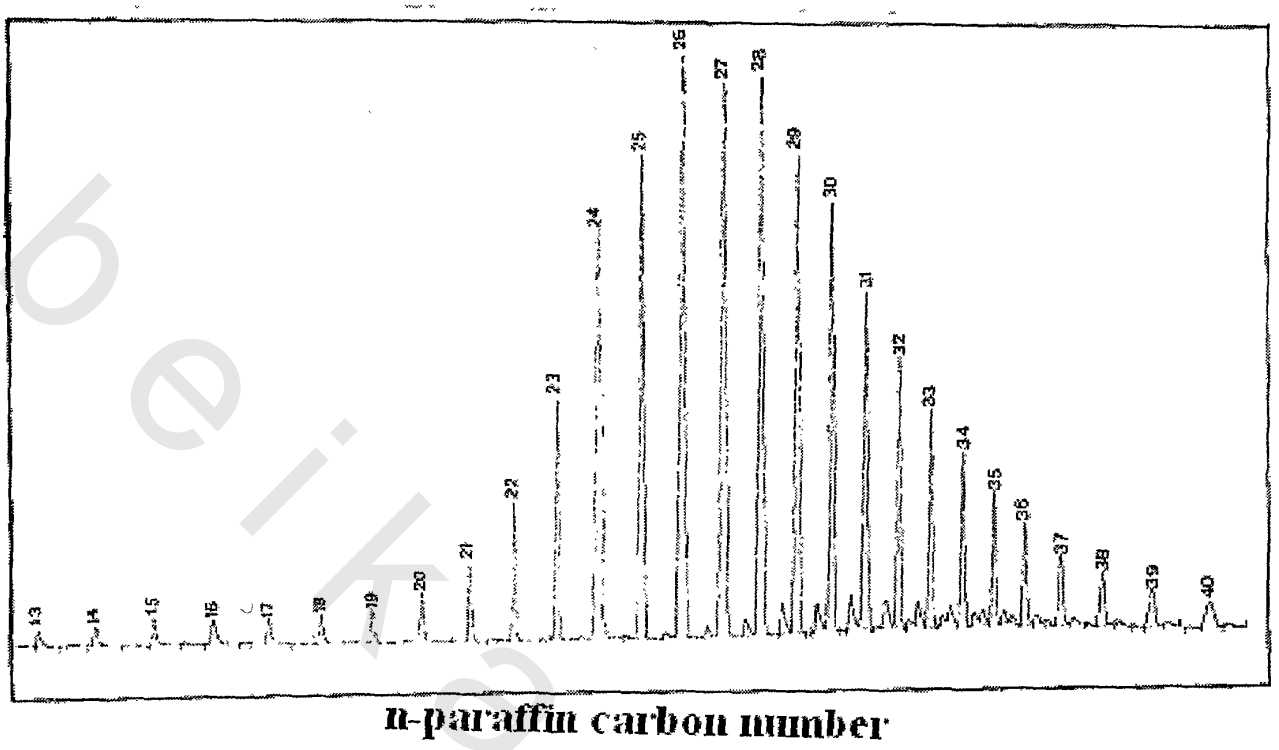
A waxy crude oil (from QPC) was used for evaluation the performance of the prepared additives as PPD to increase the flow behaviors of these crude oils. The physicochemical characteristics of BS crude oils indicate that this crude have waxy and asphaltene content as 20 and 5 wt %, respectively. Asphaltenes were isolated by IP 143 procedure using n-heptane. In addition, the paraffin content of the tested crude oil was determined by urea adduction, and then subjected to gas liquid chromatographic analysis for determination of average molecular weight distribution. The structure and composition of wax in crude oil are very important to select the suitable structure of wax dispersant to increase its flowability. However, still in most cases the wax dispersants

having highly polar functional groups are used for improving flowability of wax crude oil. The n-paraffin content in the crude oil was found 20 wt % by urea adduction. Further analysis of n-paraffins by GLC for both BS and KARAMA crude oil was carried out to determine the carbon numbers as shown in **Figures (3.1-3.3).** From data listed in **Tables (3.1,3.2)** and **Figures (3.1-3.3),** it has been concluded that the average carbon number was 27 and 29 for both KARAMA and BS crude oils and the molecular weight distribution expressed in $W_{h/2}$ has a broad distribution. It is obvious that the concentration of 50 wt % of the n-paraffin content in the crude oil in a broad range and a high average carbon number (27.2 and 29) tends to precipitate suddenly in the form of a solid at a fairly high temperature above the pour point. These n-paraffins have the ability to construct rapidly a massive interlocking network that hinders the response of the crude to additive at a preceding stage of formation of fine crystals. Although crude oils show high specificity with respect to flow improvers, there are some common structural features among these polymeric additives. For instance, there is some relationship between the wax carbon distribution of the petroleum oil and the length of the pendant chains of polymeric additives. The complex nature of the interactions among various precipitating high molecular weight species such as asphaltenes, maltene, or resin fractions, in addition to the waxes covering a wide range of carbon numbers, has resulted in specific additives being effective only

with very specific types of crudes. The structure and composition of flow improvers should possess highly polar functional groups such as amide, ester, amine and hydroxyl groups. When an additive contains both long chain hydrocarbon and polar moieties, it can be used as wax dispersant and flow improver. Crude oil additives are chemical compounds added to the base oils to impart specific properties to the oils. Some additives impart new and useful properties to the crude oil and others enhance properties already present. It is desirable that the viscosity of the crude oil be changed with the production and transportation temperature range. Moreover, all waxy crude oils contain some dissolved wax which begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets and keep it from pouring or flowing at low temperature **[20]**.

Low pour points may be achieved by intensively dewaxing the oil during refining which decreases the oxidation stability of the oil and increases the tendency toward carbon deposits. It is desirable to add a pour point depressant to decrease the pour point of oils. This depressant may acts as anti-settling and improves the flow ability **[21]**.

The structure and composition of wax dispersants are similar to those of flow improvers in some derivatives but different in others.



Figure(3.1): GLC of n-Paraffin Distribution of KARAMA Crude Oil.

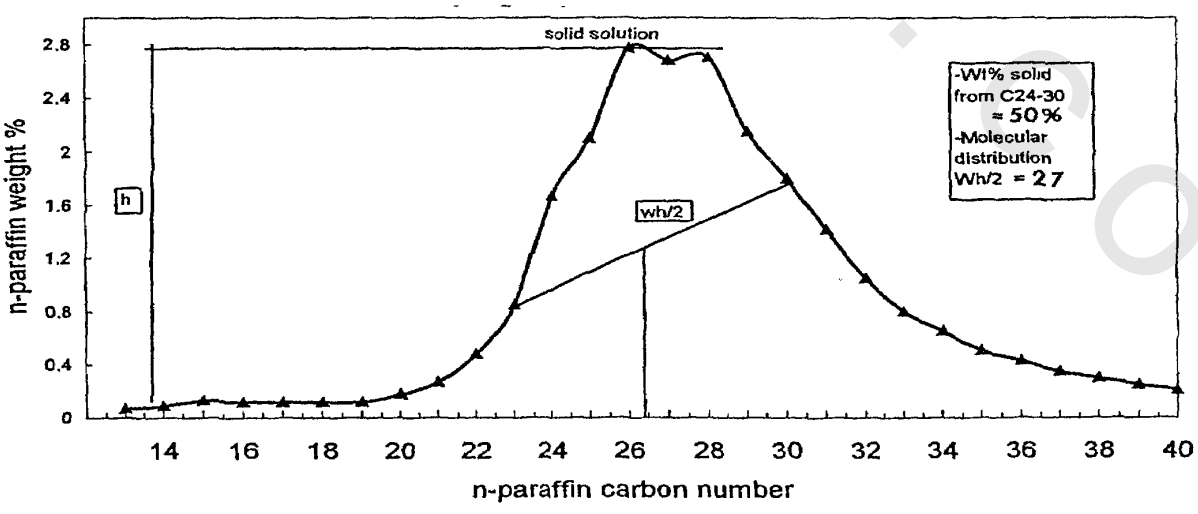


Figure (3.2): n-Paraffin Molecular Weight Distribution of KARAMA Crude Oil.

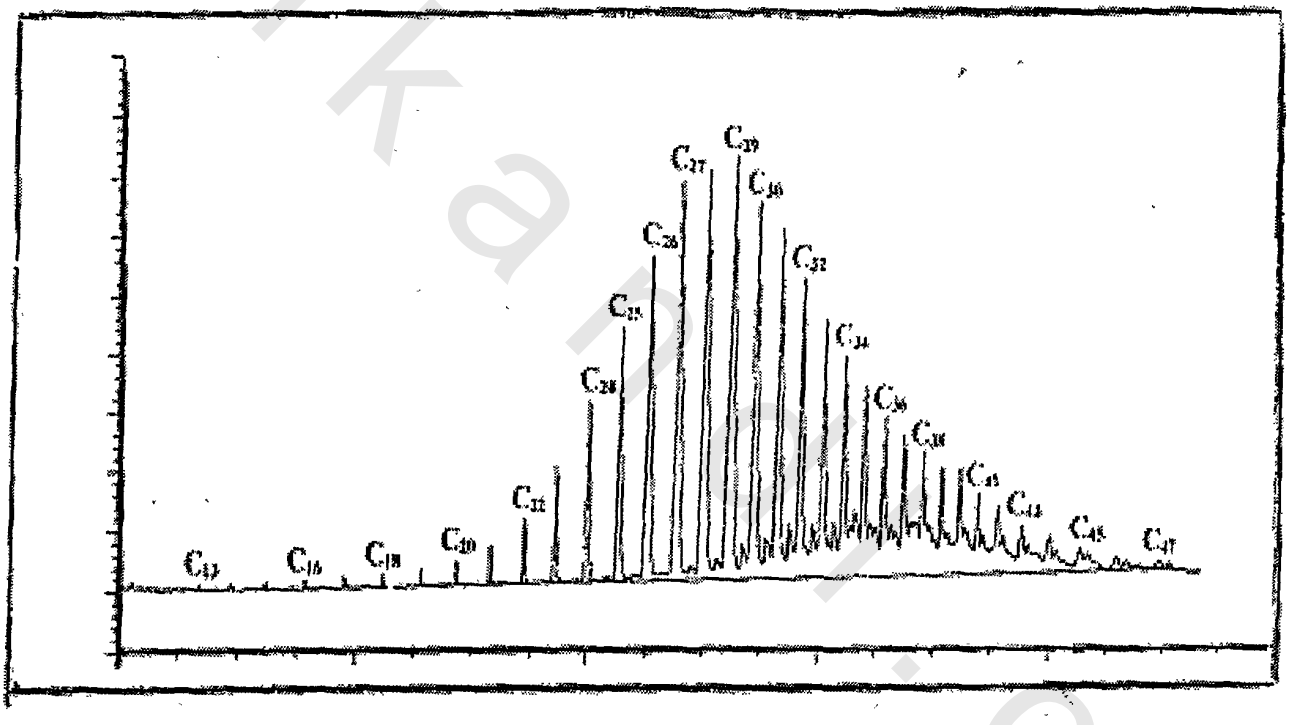


Figure (3.3): GLC of n-Paraffin Distribution of BS Crude Oil.

Table (3.1): Carbon Number Distribution of n-Paraffin Fraction Separated with KARAMA Crude.

Carbon No.	Wt%	Mwt.	No. of Moles 10^{-4}
13	0.07	184	3.804
14	0.09	198	4.545
15	0.13	212	6.132
16	0.12	226	5.309
17	0.12	240	5.000
18	0.12	254	4.724
19	0.12	268	4.477
20	0.18	282	6.382
21	0.27	296	9.121
22	0.48	310	15.483
23	0.85	324	26.234
24	1.67	338	49.408
25	2.10	352	59.659
26	2.77	366	75.683
27	2.68	380	70.526
28	2.70	394	68.527
29	2.15	408	52.696
30	1.80	422	42.654
31	1.42	436	32.568
32	1.05	450	32.333
33	0.80	464	17.241
34	0.65	478	13.598
35	0.51	492	10.365
36	0.43	506	8.498
37	0.35	520	6.730
38	0.30	534	5.617
39	0.25	548	4.562
40	0.21	562	3.736
Total	24.39		636.612

Total Paraffin Content=n-paraffin wt%+ iso-paraffin wt%
Average Mwt= wt %/ No. of moles
Average Carbon No.= C_nH_{2n+2}
n=27.2

Table (3.2): Carbon Number Distribution of n-Paraffin Fraction Separated with BS Crude.

Carbon No.	Wt%	Mol Wt.	No. of Moles 10^{-4}
13	0.0115	184	0.6247
14	0.0178	198	0.8992
15	0.0216	212	1.0226
16	0.0235	226	1.0395
17	0.0292	240	1.2149
18	0.0354	254	1.3936
19	0.0405	268	1.5102
20	0.0615	282	2.1801
21	0.0958	296	3.2378
22	0.167	310	5.4072
23	0.1125	324	10.7505
24	0.6792	338	20.0939
25	1.2383	352	35.1925
26	1.9636	366	53.6497
27	2.8519	380	75.0496
28	3.0075	394	76.3314
29	3.0931	408	75.8096
30	2.5449	422	60.3068
31	2.1423	436	49.1342
32	1.5109	450	33.5745
33	1.1784	464	25.3953
34	0.8781	478	18.3685
35	0.68104	492	13.8425
36	0.5523	506	10.9161
37	0.4451	520	8.5585
38	0.3121	534	5.8427
39	0.3878	548	7.0751
40	0.2768	562	4.9236
41	0.2101	576	3.5583
42	0.1972	590	3.3422
43	0.1607	604	2.6594
44	0.1571	618	2.5409
45	0.1336	632	2.1135
46	0.0945	646	1.4641
47	0.0845	660	1.2808
Total	25.6281		620.3022

Total Paraffin Content=n-paraffin wt%+ iso-paraffin wt%
Average Mwt= wt %/ No. of moles
Average Carbon No.= C_nH_{2n+2}
n=29.3

Hence, one chemical structure may provide the function of the two additives by holding extra specific polar groups, but still in most cases two- or even three-component additives are used for improving flow ability **[23- 24]**. Among the various polymeric additives employed in modern engine, one of the most important is the type, which acts to lower the pour point. When an additive comprising two components is used as pour point depressant, one component serves as the conventional polymeric flow improver while the other component, including mainly a hydrocarbon-oil-soluble nitrogen-containing compound, acts as wax dispersant.

3.2. SYNTHESIS OF ADDITIVES

3.2.1. Preparation of Rosin Derivatives

Direct esterification and amidation of carboxylic acid groups of rosin acids were carried out to prepare the rosin ester and amide. In the present study, the PEG and Nafol 20^{+} were used to prepare the rosin monoester, where the hexadecylamine was used to prepare the rosin amide. The diesters of rosin acid were based on the rosin maleic-anhydride adduct. The carboxylic and anhydride groups are used as reactive sites in the esterification reaction. The structures of the produced rosin esters were determined by using ^{1}HNMR spectroscopy. The ^{1}HNMR spectra obtained from the esterification and amidation of rosin acid were represented in **Figure (3.4 a-d)**. It can be noted that the disappearance of signals at 8.5 ppm assigned to COOH group of rosin acid **Figure (3.4 a)**

and appearance of new peak at 4.2 ppm in spectra of rosin- Nafol 20^{+} and rosin-PEG ester, **Figures (3.4 b, c)**, indicate the formation of ester for rosin acid. The appearance of peak at 3.5 ppm, assigned O=CNH group instead of peak at 8.5 ppm **Figure (3.4 d)**, indicate the formation of amide from rosin acid and hexadecylamine. The new peak at 3.6 ppm in spectra of rosin-PEG 1000, referred to OH group of PEG indicated the formation of rosin-PEG 1000 ester **[124]**.

The FTIR spectra of rosin-maleic adduct, rosin-PEG- Nafol 20^{+} and rosin - Nafol 20^{+} diester were recorded in **Figures (3.5 a, b and c)**, respectively. In **Figure (3.5 a)**, the absorption peaks due to unsaturated carbon were observed at 3086 cm^{-1} for the olefinic =CH stretching, at 1580 cm^{-1} for the C=CH stretching, and peak at 990 and 930 cm^{-1} , respectively. The C=C out of plane (bending) indicates the presence of unconjugated C=C as the formation of rosin maleic-anhydride adduct **[125]**. Basically, the same characteristic features were observed in the FTIR spectra, which recorded for the other two Rosin maleic diester. FTIR spectra of the resulting rosin maleic diester **Figures (3.5 b, c)** showed no absorption lines for anhydride groups, and thus it was assumed that, the esterification reaction was completed successfully. This can be proved by appearance of one peak at 1750 cm^{-1} in spectra of rosin-PEG- Nafol 20^{+} and rosin- Nafol 20^{+} diester, as shown instead of two peaks at 1810 and 1780 cm^{-1} which characterize the O=C-O-C=O stretching of anhydride group.

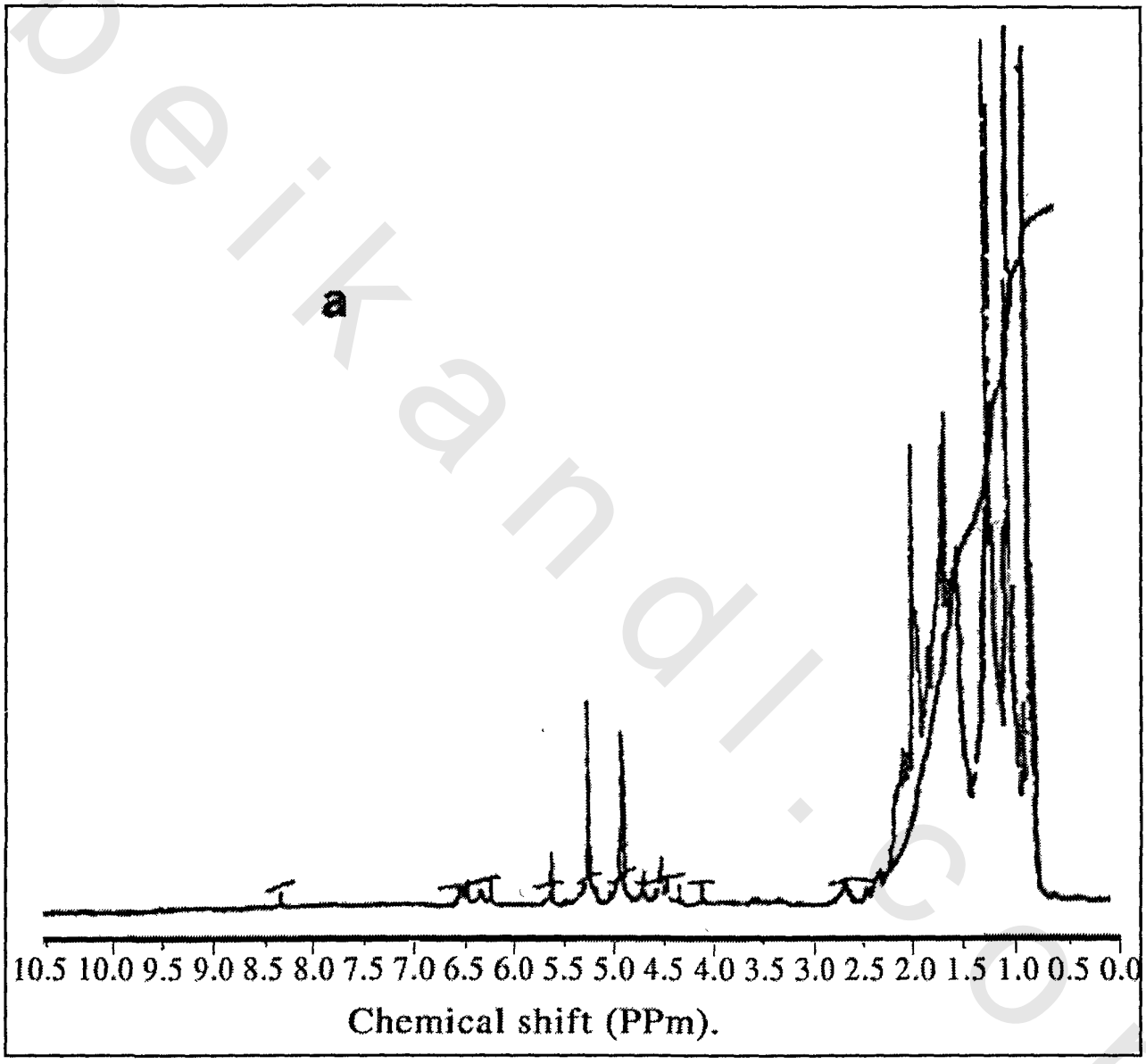


Figure (3.4a): ^{1}HNMR Spectrum for rosin acid

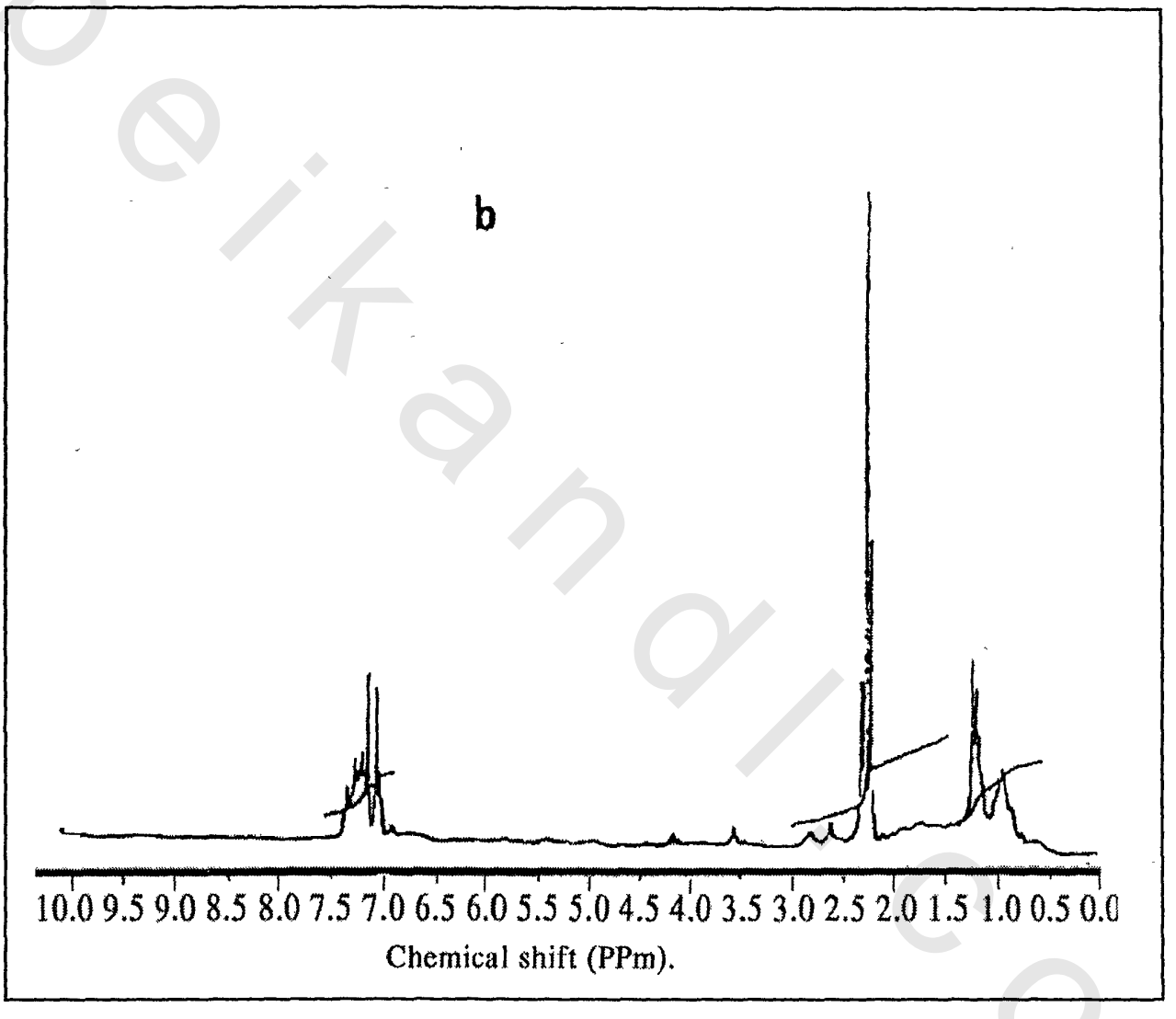


Figure (3.4b): ^{1}HNMR Spectrum for rosin acid- Nafol 20^{+} ester.

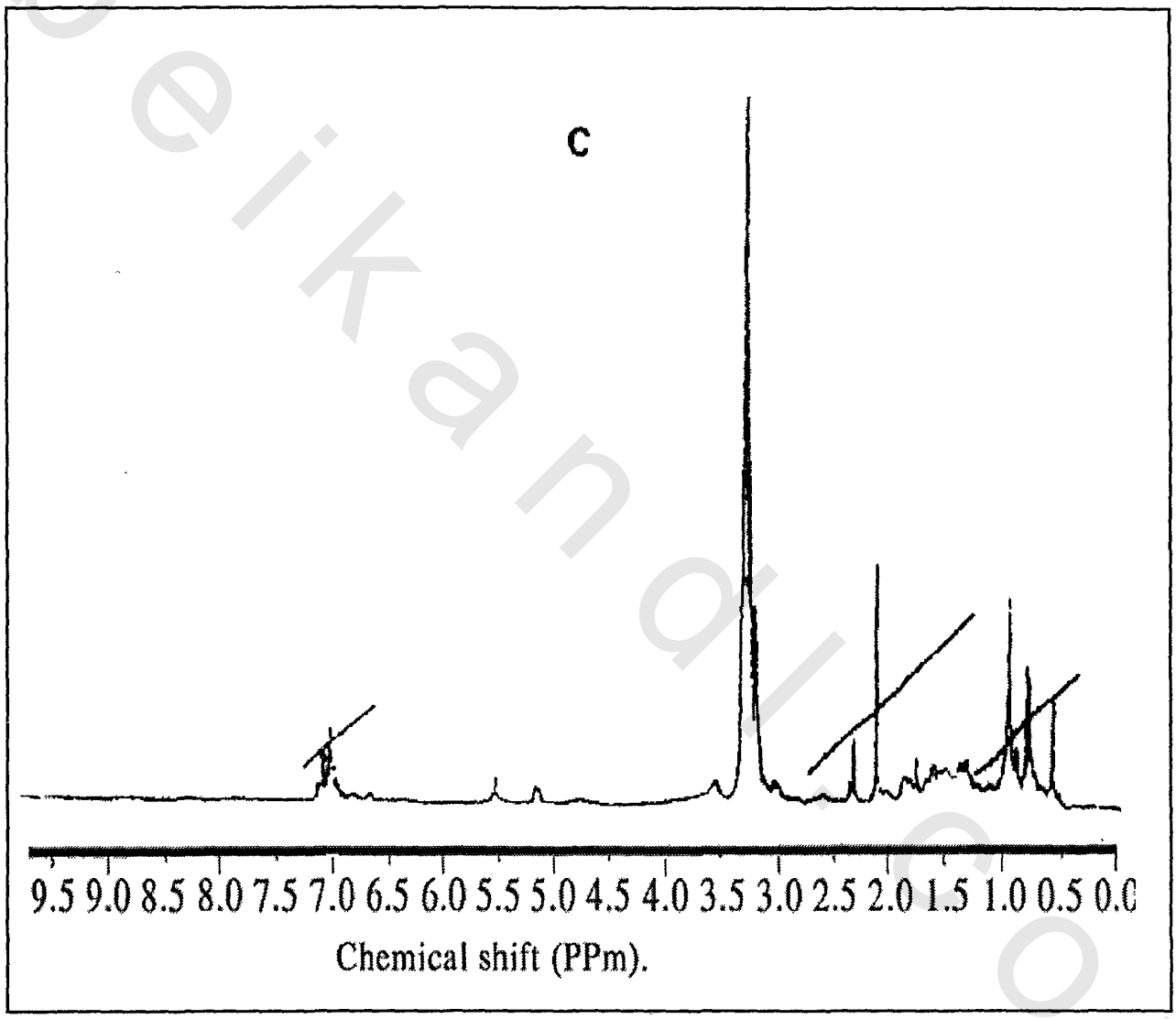


Figure (3.4c): ^{1}HNMR Spectrum for rosin acid- PEG ester

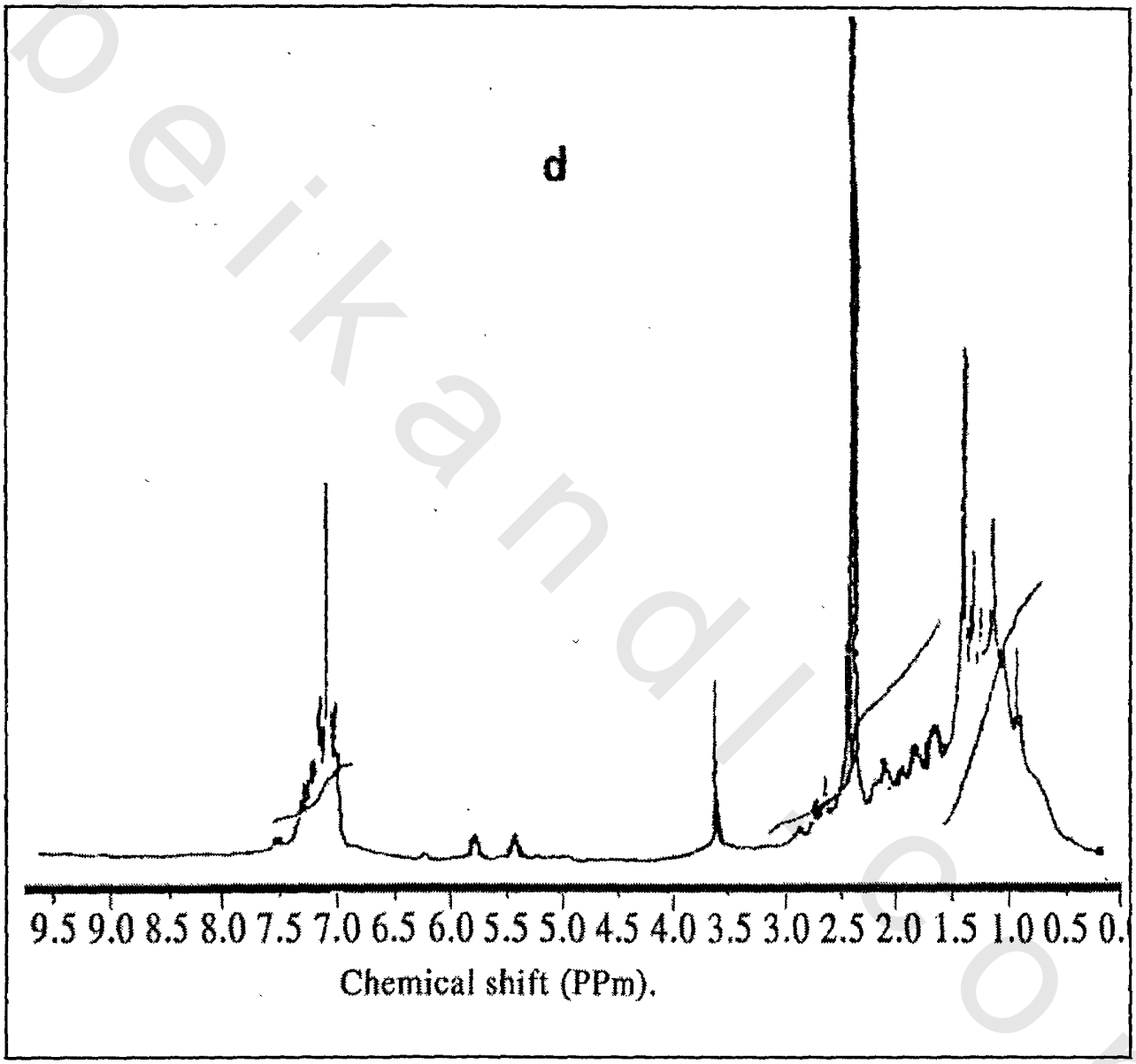


Figure (3.4d): ^{1}HNMR Spectrum rosin acid- amide.

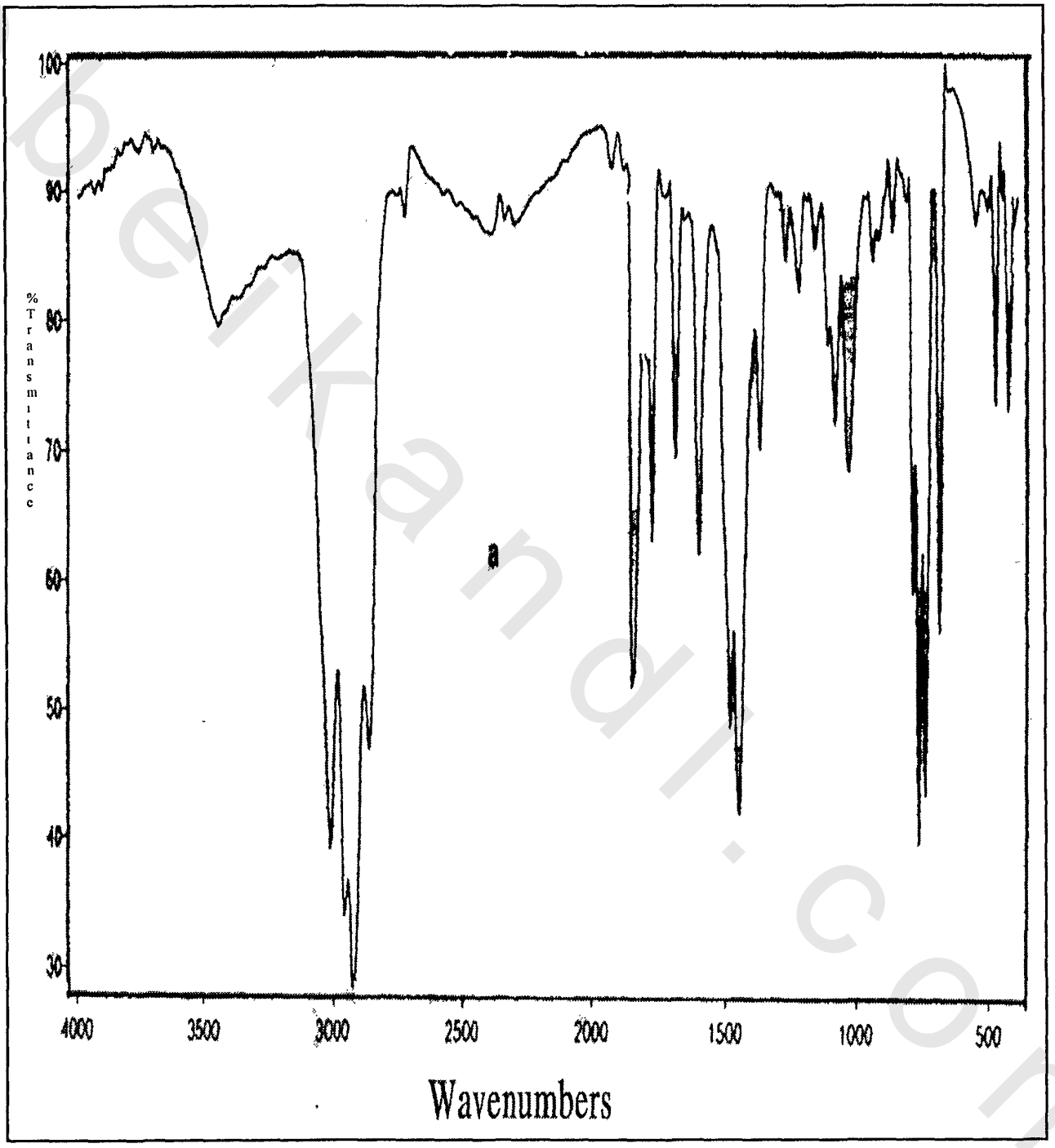


Figure (3.5a): IR Spectrum for rosin acid- maleic anhydride adduct

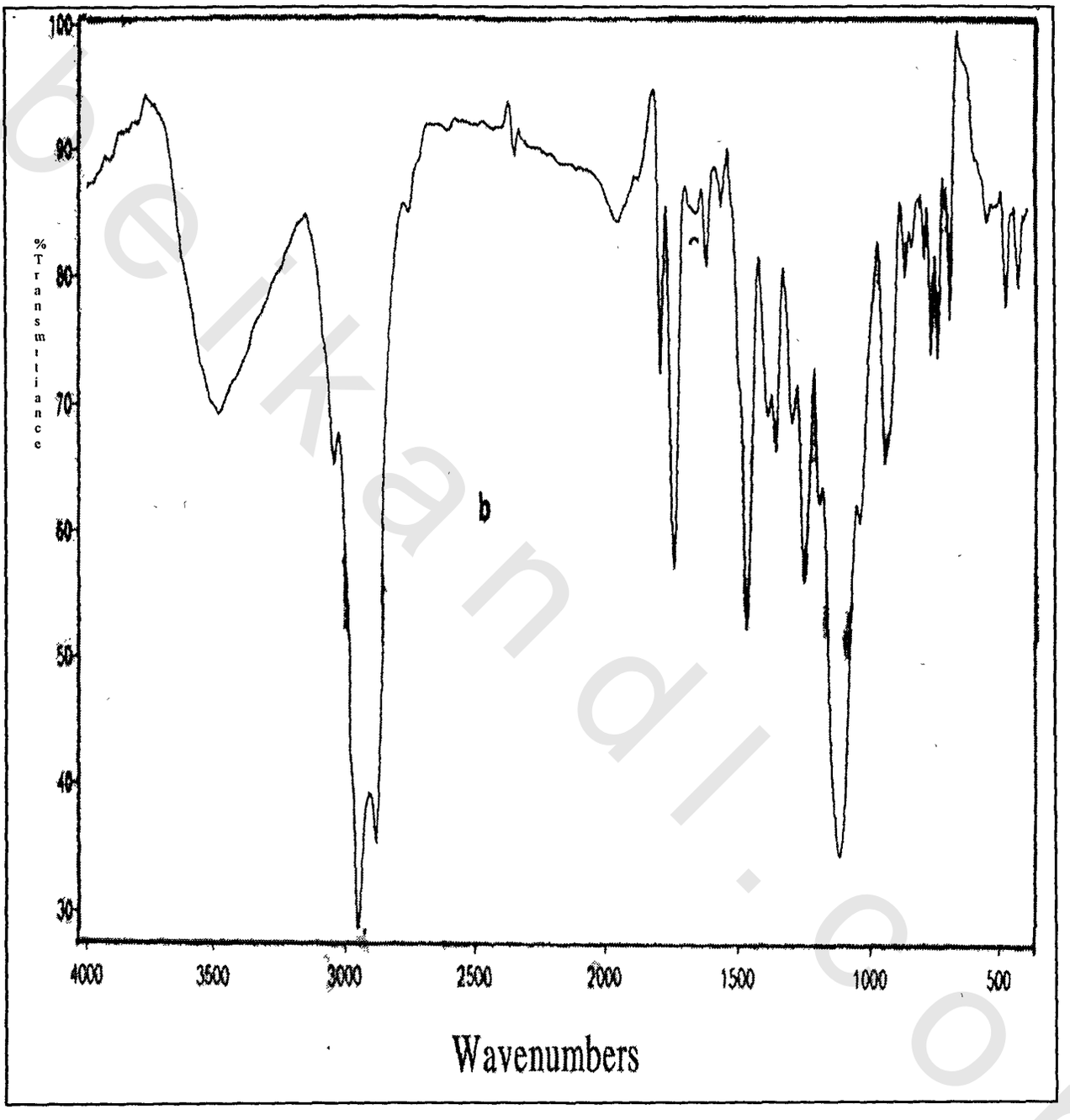


Figure (3.5b): IR Spectrum for rosin acid adduct ester of (Nafol 20^{+}-PEG)

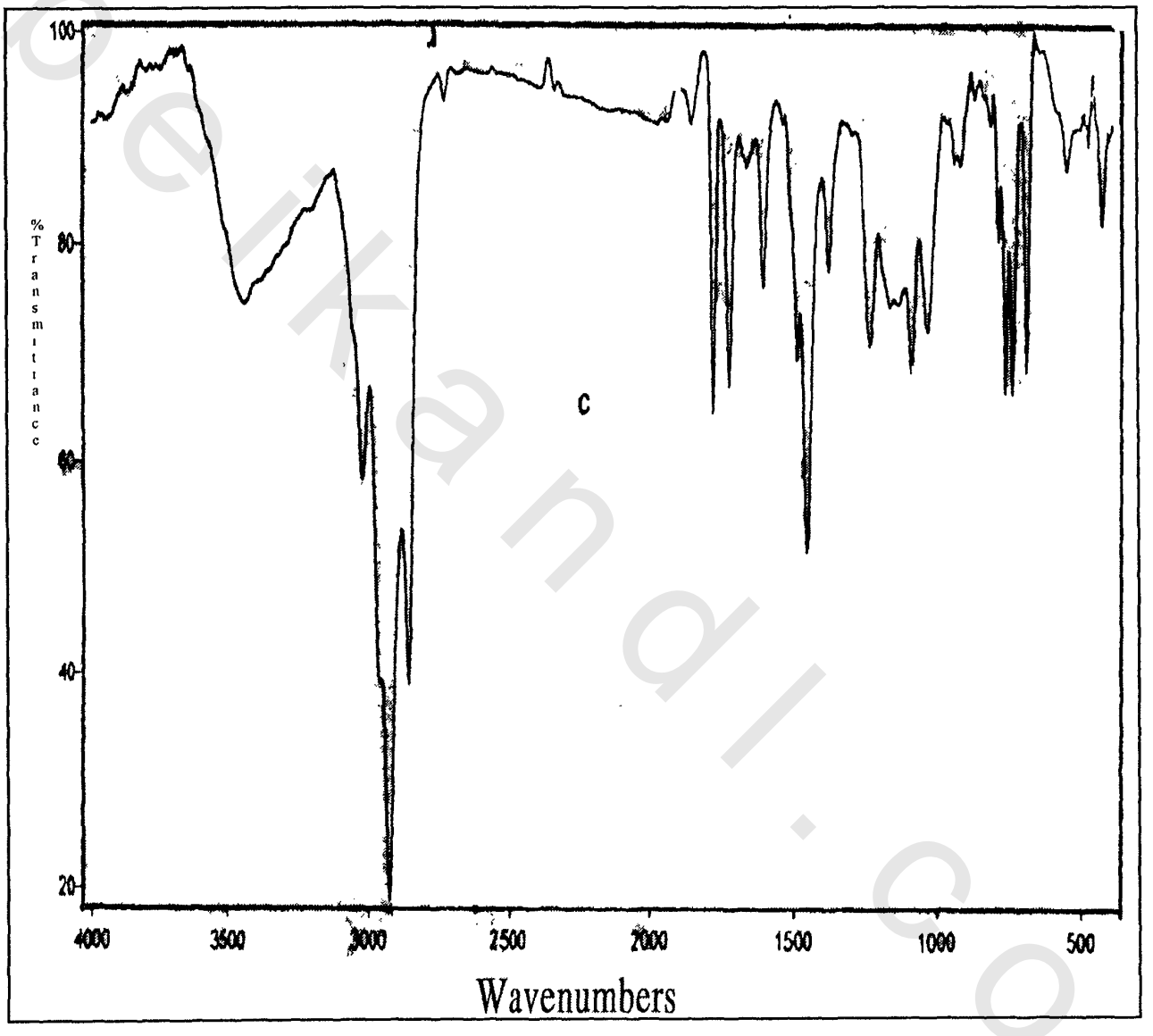


Figure (3.5c): IR Spectrum rosin acid adduct diester with Nafol 20^{+}.

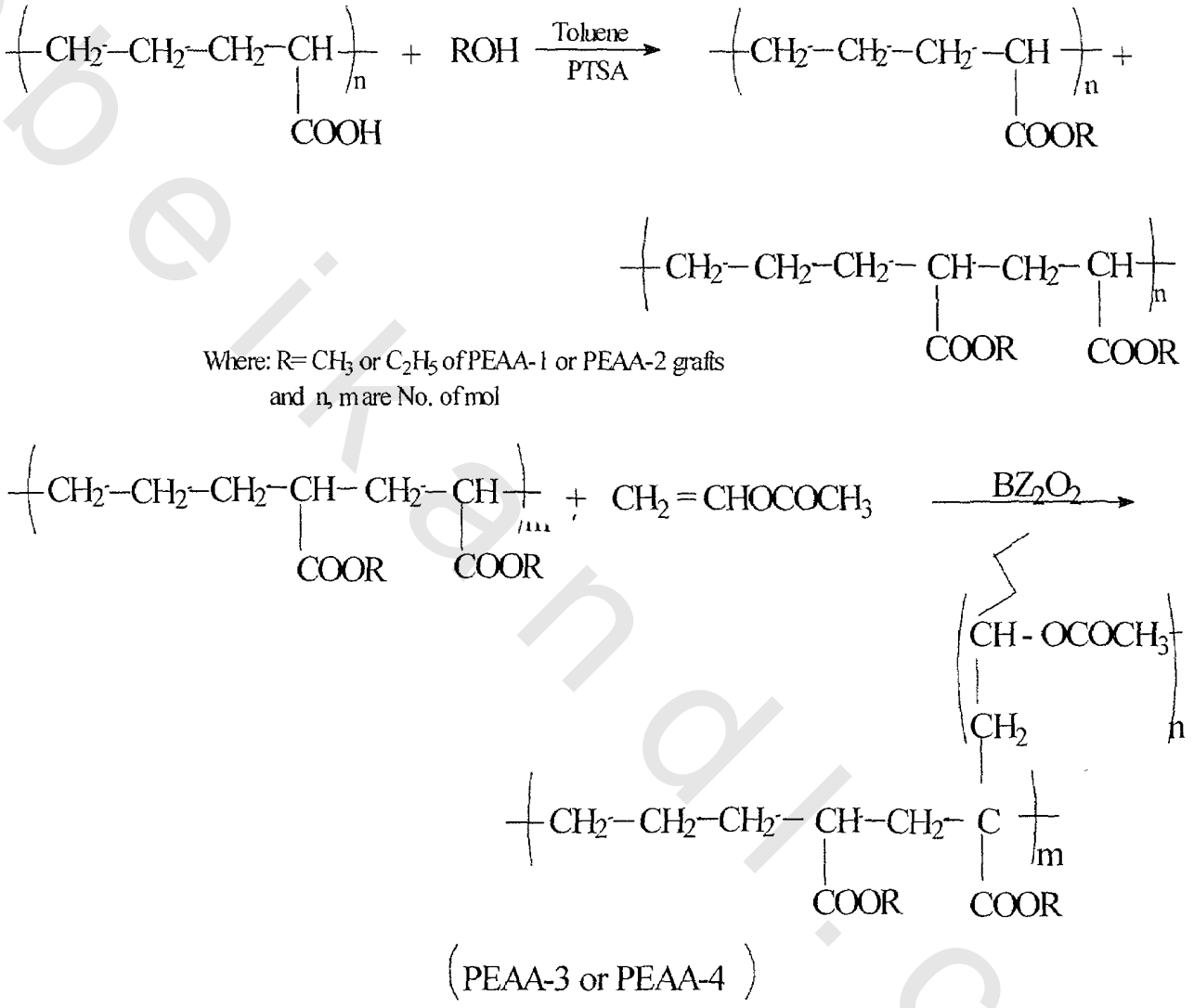
3.2.2. Grafting of PEAA Copolymers:

It is of considerable interest, in recent years, to develop new materials from waste polymeric materials either by chemical modification **[126-128]** or polymer recycling **[129,130]**. The chemical modification of recycled polymer materials is based on grafting technique **[131]**. Early attempts to produce graft copolymers by cationic methods utilizing metal halides, $AlCl_3$, $SnCl_4$ or BF_3 **[132]**, have been used it initiate cationic polymerization of a variety of monomers from numerous polymer backbones. An additional useful terminology concerns the synthesis of grafts **[133]**, grafting onto, occurs if a growing polymer chain attacks another polymer to form branched backbone.

Polyethylene (PE) is one of the most widely used thermoplastics coating materials, which protects steel from corrosion by providing a barrier to oxygen, water and corrosive ions. Generally, plastics that contain polar function groups can be used to increase adhesion of PE with steel. These polymers include methacrylic-acid modified- polyethylene **[134]** or maleic anhydride- grafted polyethylene **[135]**. These polymers can be modified by reaction of its acid or anhydride groups to produce graft copolymer **[126]**. The present work aims to prepare graft copolymers soluble in petroleum crude oil to be evaluated for improving flow properties of petroleum crude oil. In this respect, PEAA was esterified with ethanol and methanol in presence of toluene as solvent at 90 °C

for 6h to produce PEAA-1 and PEAA-2 copolymers. The PEAA-1 ester was grafted with vinyl acetate monomer (30 wt % in presence of 0.2 wt % of BZ_2O_2) in N_2 atmosphere using Diesel fuel as solvent at 65 °C for 6h. The produced graft copolymer is designed as PEAA-3. These additives were designed as PEAA-1, PEAA-2 , PEAA-3 and PEAA-4 when ethanol, methanol, ethanol with vinyl acetate and methanol with vinyl acetate were used as grafts, respectively. The reaction scheme is given in **Scheme (3.1)**. The grafting have been utilized by esterification with using the carboxylic acid groups of ethylene acrylic acid copolymer as reactive sites in reactions with ROH. It was reported that, PEAA is a semi-crystalline polymer similar to polyethylene, with a melting point of 98°C **[135]**. The PEAA used as a backbone in our experiments had an acrylic acid content of 6 mol %, and a number – average molecular weight of 16000 according to GPC measurements and data sheet of material as recorded in experimental section. The carboxylic acid groups of PEAA are intermolecular hydrogen bonded, and this fact, in addition to the effects of the crystalline morphology of the polymer, makes a true solution difficult to obtain. The PEAA waste products will swell strongly at room temperature in a polar solvent such as methyl ethyl ketone, and will be a true solution only at the boiling in toluene at 90 °C, and in order to obtain high reaction rates we choose these conditions to carry out the esterification reactions.

The reaction conditions to obtain PEAA grafts were reported in experimental section. In this respect, esterification of methyl and ethyl alcohol with –COOH groups of PEAA was completed separately to produce esters having one type of ester groups and to determine the reactivity of each group towards PEAA. The accessibility and reactivity of the functional groups may limit the esterification reaction rates. In the present case, the reactive carboxylic acid groups are relatively few, for instance, one-group equivalent 35 methylene units in the backbone, and, consequently, the reaction rates should be rather low. The low rate can be compensated for by increasing the concentration of hydroxyl groups, but because a content of alkyl ester less than 50% by weight was wanted, the amounts of hydroxyl compounds was kept relatively low. OH/COOH ratios of 0.4 to 1 were used. All prepared of PEAA esters were soluble in toluene. The polymers were regarded as soluble if they gave clear solutions with no residues after 24 h. The solubility of the graft copolymer was found to depend on the molecular weights as well as on the number of grafts side chains connected to the hydrophobic backbone. In this respect, the solubility of the prepared grafts in toluene was increased with high content of side chains and with decreasing molecular weight of the side groups. All graft copolymers, have to be purified before characterization.



Scheme (3.1): Scheme of Grafting of PEAA Copolymers.

The method of purification was described in experimental section is quite efficiency to obtained pure polymers, which can be used to calculated the yield of reactions. The purified copolymers were analyzed by FTIR spectroscopy. Spectra of the PEAA backbone and a purified grafts copolymer sample are shown in **Figure (3.6a-c)**. In this respect, the spectra of PEAA, PEAA-1, and PEAA-2 were selected as representative sample as shown in **Figure (3.6 a-c)**, respectively. In this respect, increasing of peak intensity at 1735 cm^{-1} and decreasing of peak intensity at 1700 cm^{-1}, which represent C=O stretching of ester group and carboxylic groups, indicates the conversion of carboxylic acid groups into ester groups. Furthermore, the appearance of strong peak at 1100 cm^{-1} in all spectra, C-O vibration, indicates the formation of ester grafts for PEAA copolymers. On the other hand, the disappearance of the broad peak at 3450-2800 cm^{-1} (–OH stretching of COOH group) can be attributed to the formation of ester groups for all grafts. Copolymer composition was determined by means of IR spectroscopy. To determine the VA contents in copolymers having < 20 mol% VA, the ratio of absorbances of bands at 610 cm^{-1} (wagging COOR) and 760cm^{-1} (rocking CH_2 in Ethylene units) **[136-138]** was used. To analyses copolymer containing > 20-40 mol% VA, the absorption bands at 1372 cm^{-1} (rocking CH_3 in acetate groups) and at 2925 cm^{-1} (stretching CH_3 in E units) **[136-138]** were used. The grafting of VA onto PEAA-1 and PEAA-2 in presence of BZ_2O_2 was

illustrated in **Scheme (3.1).** The mechanism of grafting based on radical polymerization onto CH backbone group as illustrated in previous work **[139-141].** In this respect, the chemical structure of PEAA-3 and PEAA-4 can be confirmed by ^{1}HNMR analysis. The signals in ^{1}H-NMR spectra of the studied copolymers were assigned according to published data **[142, 143]**. In this respect, ^{1}HNMR spectra of PEAA, PEAA-3 and PEAA-4 are presented in **Figures (3.7 a, b and c),** respectively.

The new signals at 1.97, 4.9-5.3 and 3.8 ppm in spectra of PEAA-3 and PEAA-4, which attributed to $COOCH_3$, $COOCH_2CH_3$ and CHCO of VA, indicate that VA was grafted onto PEAA chains as represented in **Scheme (3.1).** On the other hand, the signals at 1.188 and 1.42 ppm are observed in all spectra and can be attributed to CH_2 of ethylene and VA, respectively. The presence of singlet and triplet signals at 0.812, 1.2 ppm (CH_3) in spectra of PEAA-3 and PEAA-4 indicate that COOH group of PEAA were esterified with methanol and ethanol.

3.3. EFFECT OF ADDITIVES ON POUR POINT OF THE TESTED CRUDE OILS

Hydrocarbons such as; gas-, diesel-, lubricating- and crude-oils has varying amounts of paraffins. The proportion of long chain n-paraffins, in particular, determines the cold-flow behavior of the oils.

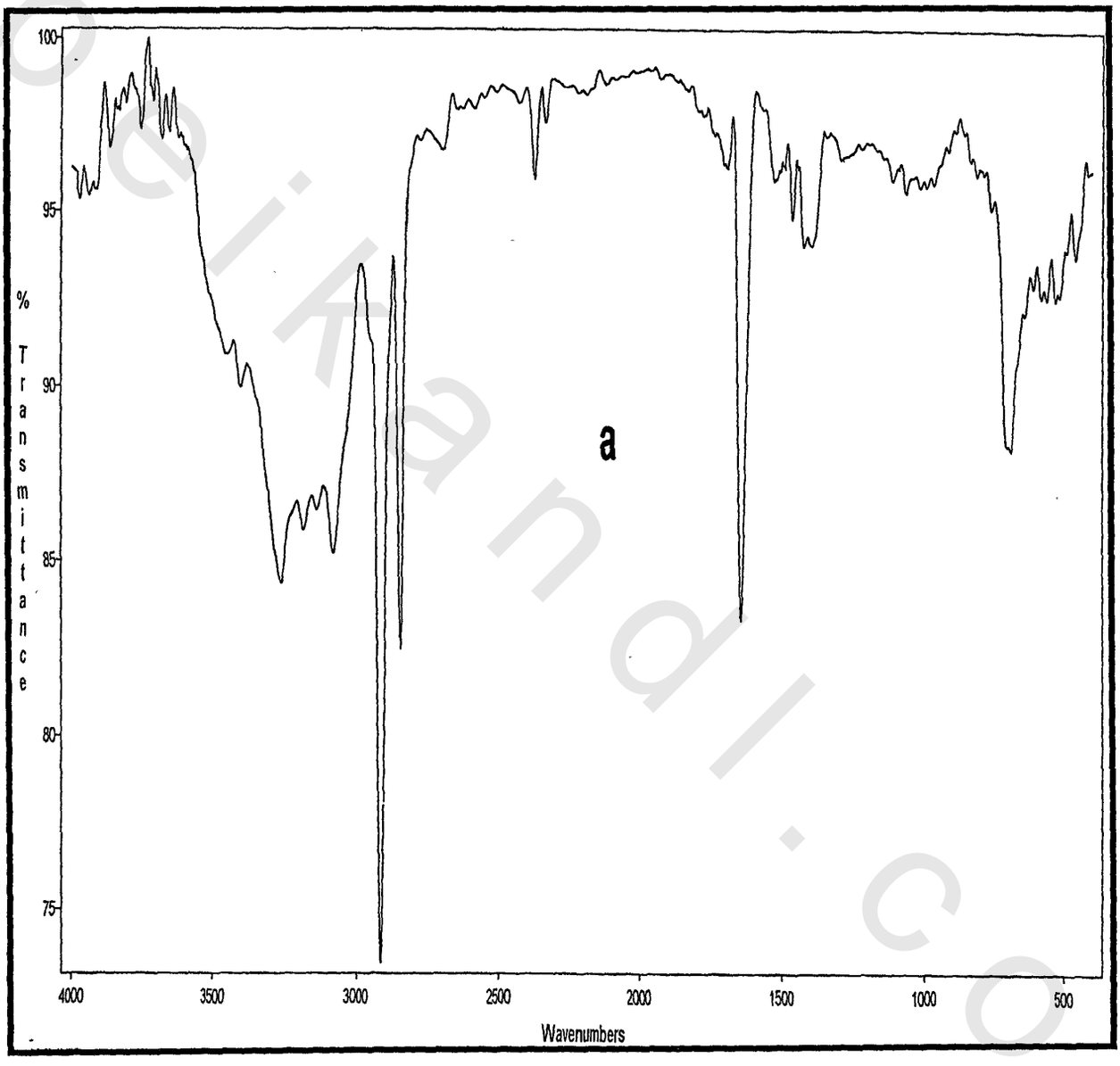


Figure (3.6a): IR Spectrum for PEAA.

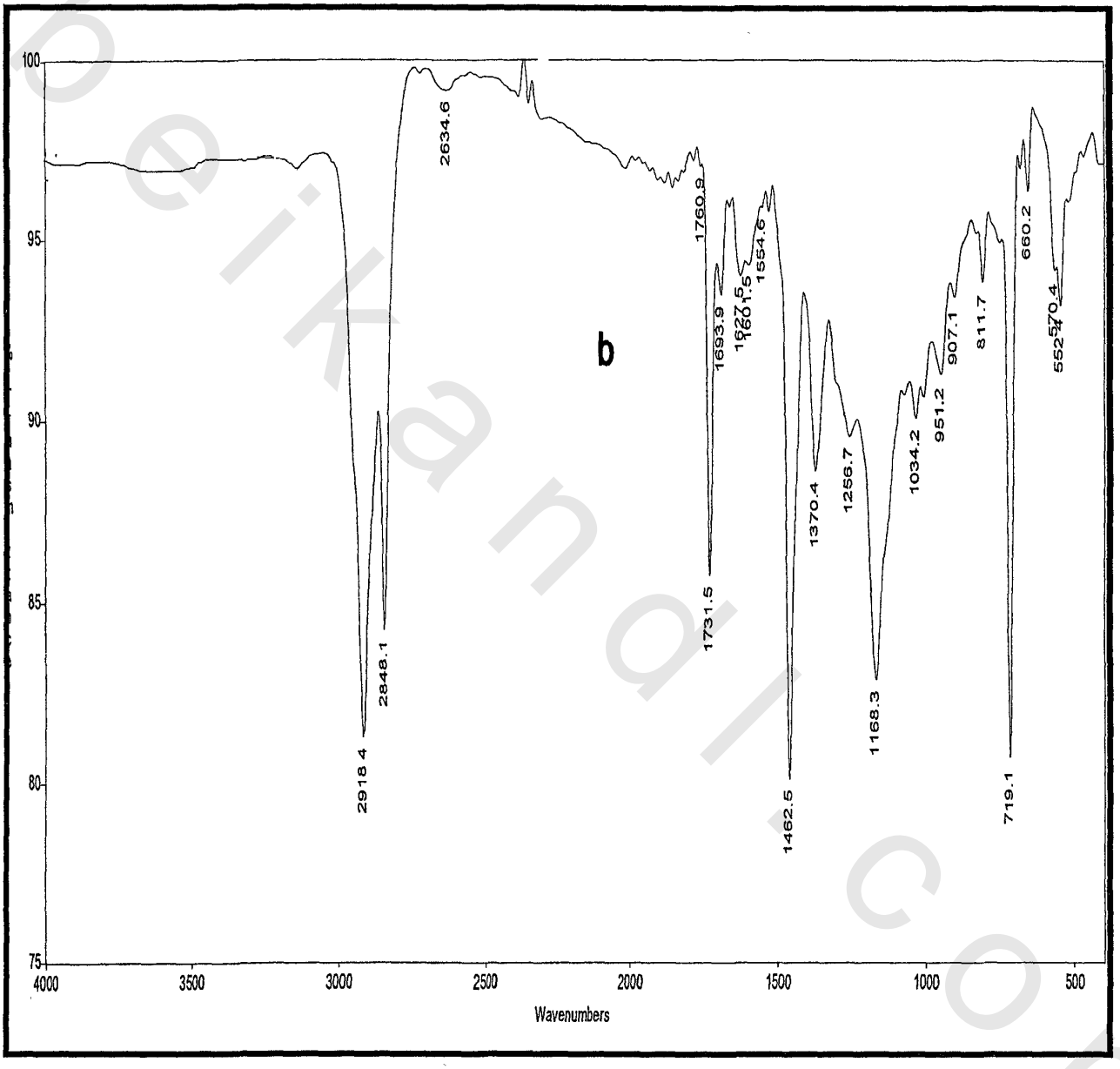


Figure (3.6b): IR Spectrum for PEAA-1.

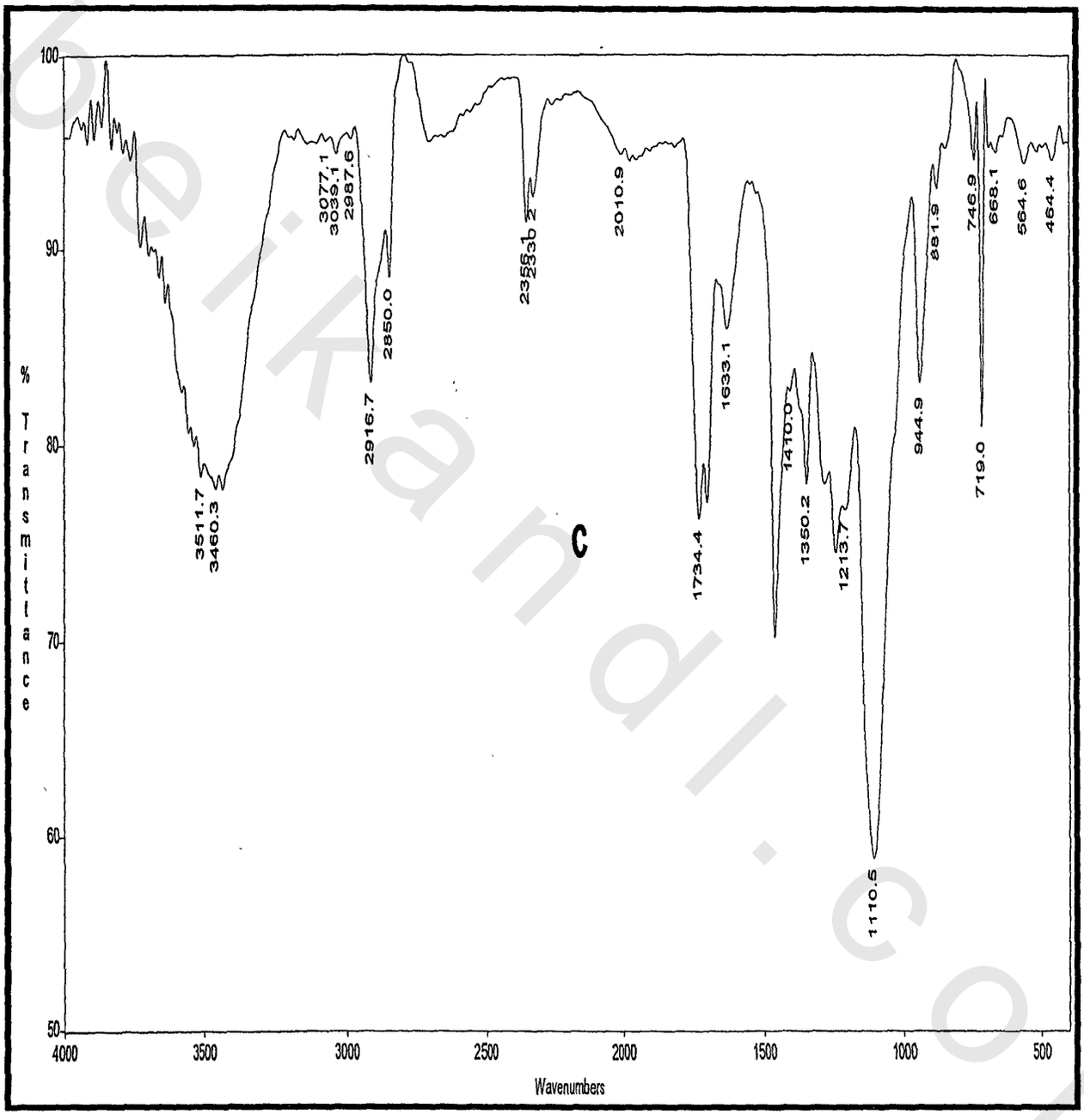


Figure (3.6c): IR Spectrum for PEAA-2.

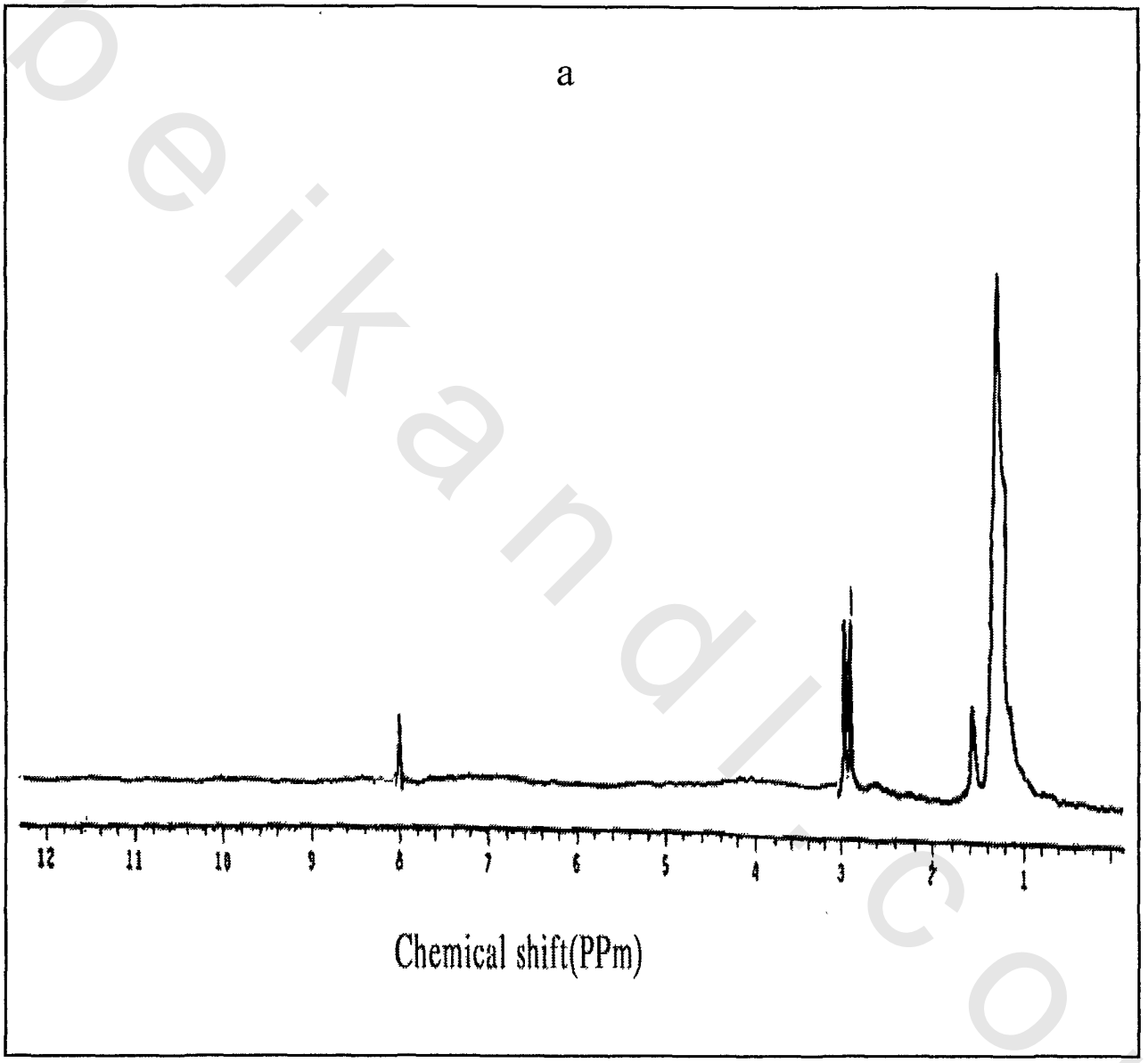


Figure (3.7a): ^{1}HNMR Spectrum for PEAA.

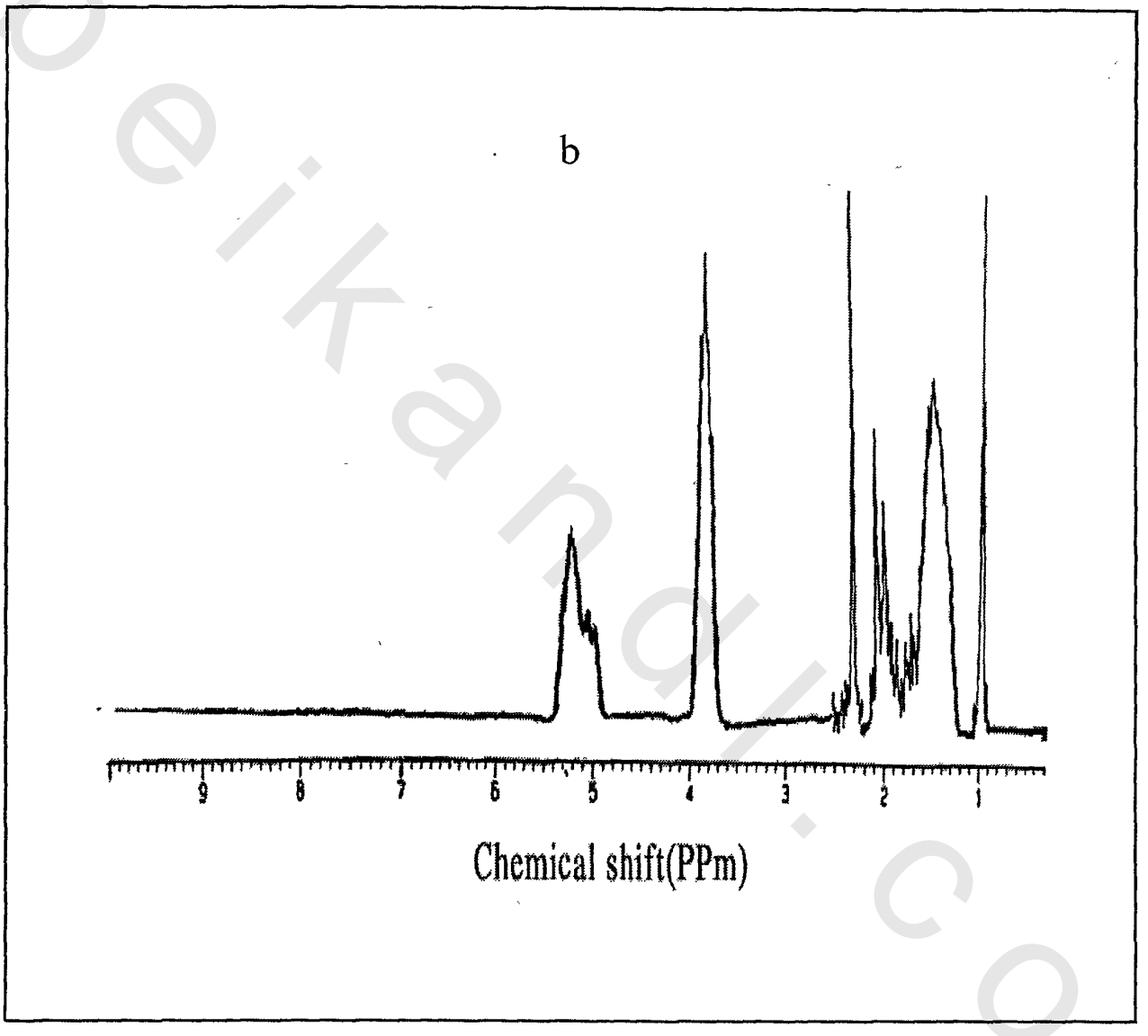


Figure (3.7b): ^{1}HNMR Spectrum for PEAA-3.

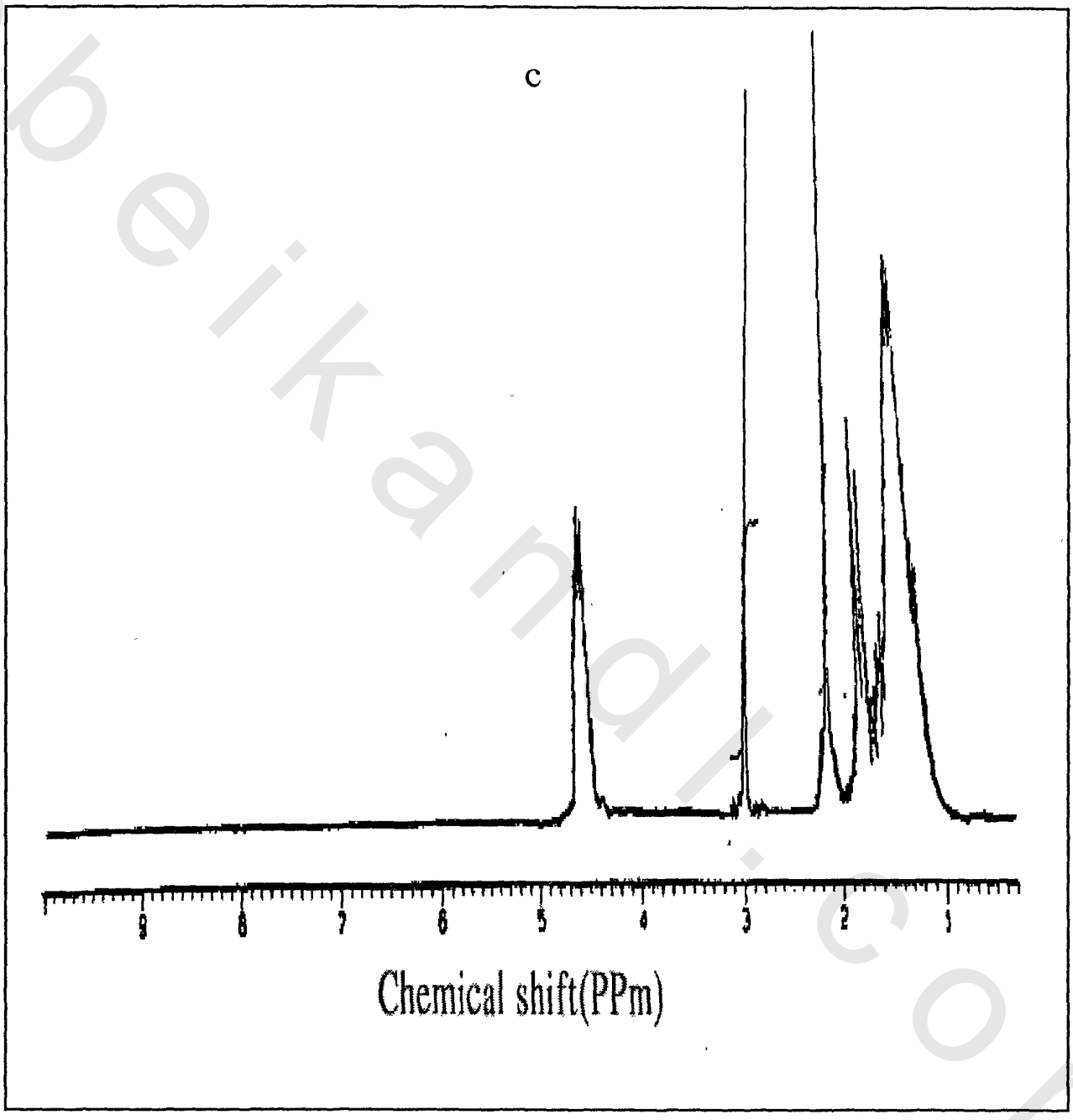


Figure (3.7c): ^{1}HNMR Spectrum of PEAA-4.

On cooling the n-paraffins separate out as plate-like crystals which interact together to form a three-dimensional network, in which still liquid oil becomes trapped, resulting to increase oil viscosity and decrease flow ability. In gas- and diesel-oil applications this phenomenon results in filter blockage, whereas in crude oil application it results in the gelatin of the crude oil and the formation of deposits in pipelines and storage tanks leading to considerable losses in production and capacity.

Some investigators **[144, 145]** reported that the acrylic and methacrylic acid copolymers with maleic anhydride could be used as flow improvers to such oils. These additive components stem from old-world wax plate modification technology have developed for improving distillate flow in pipelines and pumping system. The newer pour point depressants are working by minimize the attraction of wax crystals and modifying the shape and size of wax crystals. These additives effectively reduce the crystal formation rate and allow other flow modifiers to perform as designed **[146, 147]**. The propenoxylated tetra ethylene pentamine adduct with α-olefin-maleic anhydride copolymer show the high efficiency in improving the flow ability of both distillate fuel and crude oils **[18, 148]**. Also, the ester derivatives of maleic anhydride- vinyl acetate copolymer were evaluated as pour point depressant and as flow improver for diesel fuel **[149]**, where olefinic fatty acid ester and unsaturated olefinic amide were used as pour point depressant for waxy crude oil **[150]**.

The use of surfactants as additives for motor fuels and their functioning mechanism for combustion was reported **[151- 154]**. Possible composition and surfactant action as detergent, antifreeze, anticorrosion and protective additives to aviation fuels and jet engine fuels were considered **[151]**. The effect of anionic, and nonionic surfactants on jet length, jet contraction and drop size resulting from the formation and break up of liquid jets was investigated **[152- 154]**.

3.3.1. Effect of the Rosin Acid Derivatives on flowability of Crude Oil

The activity of the prepared rosin ester and amide derivatives as wax dispersants was evaluated on the basis of their chemical structures. The eight prepared products are (PEAA-1, PEAA-2, PEAA-3, PEAA-4, EO9, EO13, EO23, and EO91) were tested to improve the flow properties of the investigated crude oil in term of pour point depression at concentration of 50, 100, 250, 1000, 2000, 3000, and 5000 ppm. The pour point values were measured for Karama field and listed in **Table (3.3)**. In general it was observed that, increasing concentrations of additives up to 2000 ppm decreases PP values. The effectiveness of pour point depression increases in the order of EO23>EO13>EO9. The results for EO91 was nearly equal as for EO23, up to concentration 250 ppm. But at high concentration from 500 up to 5000 ppm, the worthy data were obtained. This may be due to increase of ethylene oxide length leads to coiling in the system

(crude oil), as result that, the effectiveness decreased. The relation between ethylene oxide content and the depression of pour point against different concentration in ppm was represented in (Figures 4 and 5). The date listed in **Table (3.3)** reveal that, the maximum effectiveness was observed with hexadecylamide of rosin acid (RA) and Nafol 20^{+} ester of rosin acid (RN) to lower the pour point at concentration 1000 ppm. In this respect the Δ pp for RA and RN is 9 and 6 °C, respectively. This can referred to presence of nitrogen atom in amide group may be increasing the activity of RA to improve the flowability of the crude oil. This finding runs in harmony with the pervious work **[149]**. Meanwhile, Nafol 20^{+} diester of rosin maleic anhydride adduct (RM-2N) exhibits maximum depression of pour point at 2000 ppm (Δ pp is 12 °C) the ethoxylates and Nafol 20^{+} ester (EO23-MN) show a maximum effectiveness of pour point depression at 1000 ppm (Δ pp is 15 °C). This behavior can be referred to the presence of ethylene oxide units in addition to the Nafol 20^{+} ester.

The interaction of these compounds with crude oil may occur through well matching of alkyl chain and polar groups of abietic with that of n-paraffin of crude oil. On the other hand, the presence of polyoxyethylene units introduces ethereal polar groups to the additives. These polar groups may reach a surfactant character, which is considered as the basic prerequisite for the dispersant potential. The data in **Table (3.3)** show that the EO23 exhibits maximum efficiency among EO91, EO13 and EO9

toward PP depression. The data in **Table (3.3)** indicate that the EO23 possess the better surface properties among other ethoxylated compounds (EO9, EO13 and EO91). The structure and composition of wax in crude oil are very important to select the suitable structure of wax dispersant to increase its flowability. However, still in most cases the wax dispersants having highly polar functional groups are used for improving flowability of wax crude oil. The n-paraffin content in crude oil was found 20.0 wt% by urea adduction. Further analysis of n-paraffins by GLC was carried out to determine the average molecular weight and molecular weight distribution in terms of carbon numbers as shown in **Figures (3.1-3.3)**. From data in **Tables (3.1-3.2)** and **Figures (3.1-3.3)** it has been concluded that the average carbon number was 27.2 and the molecular weight distribution expressed in $W_{h/2}$ has a broad distribution. It is obvious that the concentration of 50 wt% of the n-paraffin content in the crude oil in a broad range and a high average carbon number (27.2) tends to precipitate suddenly in the form of a solid at a fairly high temperature above the pour point. These n-paraffins have the ability to construct rapidly a massive interlocking network that hinders the response of the crude to additive at a preceding stage of formation of fine crystals.

It was observed that the prepared rosin derivatives failed to decrease pour point of BS crude oils even at high dose.

Table (3.3): Effect of Concentration Additives on the Pour Point of QPC Crude Oil.

Sample Additive	Conc. PPm	Pour point (PP)	ΔPP
Blank	0.0	27	-
EO9	250	21	6
	500	21	6
	1000	21	6
	2000	18	9
	3000	27	0
	5000	30	-3
EO13	250	21	6
	500	21	6
	1000	21	6
	2000	21	6
	3000	27	0
	5000	30	-3
EO23	250	21	6
	500	18	9
	1000	15	12
	2000	15	12
	3000	27	0
	5000	33	-6
EO91	250	21	6
	500	24	3
	1000	24	3
	2000	24	3
	3000	27	0
	5000	33	-6

Accordingly, the aim of the present section was directed to solve this problem by using new polymer blends derived from plastic waste. The produced copolymers of PEAA grafts were blended with same weight percentage of rosin amide and solublized in Diesel fuel with concentration of 10 wt %.

The calculated concentration of additives with ppm was based on total weight of polymer solution including both polymer and additives.

3.3.2. Effect of the PEAA Grafts on flowability of Crude Oil:

The physicochemical properties of the produced additives, such as density, flash point, viscosity Centipois (cP) and total concentration, were determined and listed in **Table (2.5).** Normally the average molecular weight of the commercial available pour point depressants for crude oil is 17,000. These polymers and copolymers are easily soluble in crude oil and have viscosity value below 400 Centi stock (cSt) at 50 ^{o}C to convince QPC requirements. The high wax crude oils are characterized by high pour point, high viscosity, high gel strength, and abundant wax deposits. It is well known that, as the paraffin wax content increases in crude oil, this leads to difficult solubility of wax in oil, in some cases forming a separate solid phase. The result is an increase in pour point, i.e., if the pour point of the crude oil becomes higher than the ambient water temperature, the oil

become solid or semisolid and thus nondispersible. Most of the Egyptian western desert crudes are waxy in nature.

The amount of wax constituents in these crudes may reach 20 wt % which affect their transportation at low temperatures due to wax separation. Wax deposition in process equipment may lead to more frequent shutdowns and operational problems. In extreme cases, wax crystals may also causes oil gel and lead to problems of restarting the pipeline. These adverse flow properties lead to wax deposition during storage, marked pressure drop during pipelining, reduced throughput and even pipeline blockage during transportation.

Chemical additives, referred as pour point depressants, flow improvers, paraffin inhibitors or wax crystal modifiers, are widely used for overcoming the problem worldwide. These additives have received the greatest acceptance due to its simplicity and economy. These additives function by one or more several postulated mechanisms, viz. nucleation, adsorption, co-crystallization and improved wax solubility, that result in the formation of smaller wax crystals with more regular shape. It is, however, generally as knowledge that the transition from the plate like forms of the waxes to dendritic or an spheruletic crystal structure accompanies the lowering of the pour point. So the flow improver additives can reduce the growth of the wax crystal and forms smaller crystals to intergrowth and interlock are greatly diminished. When the additives or flow improvers are added, they

alter the wax crystal size and shape in some manner and prevent the tendency to interlock. The flow improvers or pour point depressants act by regarding the growth of the wax crystals in the XY crystallographic plane, thereby producing smaller crystals have higher volume and surface ratio **[11]**. It appear that the flow improvers co crystallize with the growing wax crystal, leading to the formation of a fault in the otherwise compact regular wax crystal and resulting in diminished gel strength. So that by coating onto a growing wax crystal, the flow improvers reduces the tendency of wax crystals to interlock.

Polymers such as vinyl acetate copolymer, acrylate copolymer and their derivatives **[155]** are the main additives used to improve the flowability of very waxy crude oil, diesel fuel and other base oils at low temperature. It should be noted that polymer additives are not equally effective with the various crude oils, nor are they necessarily effective at all **[156, 157]**. It is presumed that effective additives have a good match between the polymer and crude **[158],** such as , composition and content. However, how the polymer flow improver works is not clear. Usually, more attention has been paid to the interaction of the polymer flow improver with wax **[159].** Inhibition of wax crystallization is considered to occur in the presence of polymer **[160, 31]** by nucleation, co-crystallization or adsorption. The development of additives to improve the low temperature flow properties of crude oils involves major difficulties due to complex composition of these

oils. Wax, asphaltene and resin contents in crude oil play an important role in assessing their cold flow properties. Asphaltenes and resins have profound effects on solubility of n-paraffins. The paraffin and microcrystalline waxes are present in crude oil and are separated from the crude in a refinery. It is known that, the paraffin leaves the refinery with lube oil and is separated in a lube oil plant. The paraffin is a straight chain hydrocarbon having a melt point (mP) of about 49° to 71°C (120° to 160°F). The microcrystalline wax is separated from the asphalts and is higher in molecular weight and more branched than the paraffin. It has a higher mP (60° to 89°C [150° to 190°F]), which gives it better heat resistance than the paraffin. High- melting microcrystalline wax and asphaltenes govern the ultimate crystal structure. The latter appear to retard the crystallization of high melting wax. Further, it has been shown that this pour point reducing activity of asphaltenes is closely related to their state of peptization and reaches its maximum when they are on the average of flocculation. This suggests that the pour point reducing properties of the asphaltene are due to adsorption on wax surfaces. In this work, the PEAA copolymer grafts can act as asphaltene dispersants. Hence asphaltene can be adsorbed on the surface of waxes and reduce their crystallization and enhance the flow properties of these crude oils. The four synthesized copolymers of PEAA were tested for improving the cold flow properties of QPC crude oil in term of pour point depression (PPD). The additives

were added at different concentrations ranged from 100 to 10,000 ppm and tested as pour point depressants by pour point measurements. In this respect the chemical structure of additives were based on combination of two additives. PEAA grafts are based on ethylene and polar ester groups. Polyethylene moiety is a straight chain hydrocarbon resins with a chemical composition almost exactly the same as that of paraffin. PEAA is a copolymer of ethylene and acrylate ester AA, and the AA makes the PEAA polymer more polar than wax. This polarity may reach a surfactant character which is considered as the basic prerequisite for the dispersant potential **[161]**. On the other hand, the rosin amide that used based on hexadecyl amine, in formulation of PEAA additives to increase the dispersion efficiency of these additives. It is well known that, polar nitrogen containing polymers can function as wax dispersants and flow improver simultaneously in one component additive. It is also appeared, the chemical structure of rosin moiety is resembled to asphaltene moieties that have alicyclic polar groups. Accordingly, the present additives have two components; one component serves as the conventional polymeric flow improver that includes hydrocarbon backbone compatible with wax and polar dispersant group functions as a wax dispersant. The second component of rosin amide was used to be compatible with asphaltene of crude to disperse asphaltene around wax to decrease crystallization of waxes. **Tables (3.4-3.7)** show the results obtained from the pour

point measurements for QPC crude oil. A pour point reduction higher than 21 °C was achieved by adding 5000 and 10000 ppm of PEAA and HRA to the crude oil. However, the additive lost its efficiency when the PEAA grafts and HDRA were used without blending together. The data indicate that the optimum concentration to achieve pour point reduction was 10,000 ppm and after that the pour point reduction was not changed. This means that, in this concentration range, the additive cocrystallizes with the paraffin, modifying their crystals. The loss of efficiency observed at higher concentration may be ascribed to precipitation of the pure copolymer, or to wax crystallization with nucleation induced by the copolymer.

The pour point results for pure crude oils and for the crude oil containing additive (PEAA-1 to PEAA-4) are shown in **Tables (3.4-3.7)**. The additives were more efficient in reducing the pour point of the oil obtained from the Karama field. For the Benisuif field, the additives presented the following performance order: PEAA-2 < PEAA-4 < PEAA-1<PEAA-3. PEAA-3 achieves the best performance as pour point depressant at the same concentration of other additives. These behaviors can be correlated to the structure of PEAA grafts that possess methyl, ethyl and vinyl acetate moieties and its interaction with crude oil. However, as vinyl acetate content increases a solubility parameter different from that corresponding to the crude oil, it does not precipitate the sufficient amount that would be necessary to

significantly modify the wax crystals **[162]**. By analyzing **Tables (3.4-3.7)**, the crude oil from Karama has a pour point lower than that from Banisuif mix and it has less paraffin content. Consequently, the additive effect is more pronounced for the crude oil from BeniSuif.

PEAA-2 was less effective for both crude oils. For the Banisuif crude oil, PEAA-1 and PEAA-3 exhibited the best performance as pour point reducer. It seems from the results that the grafting of vinyl acetate onto PEAA copolymer has an important effect on its performance as pour point reducer.

Bilderback et.al.,**[163]** suggested three alternative mechanisms for wax inhibitors. The additive may come out of solution at a temperature slightly higher than the oil wax appearance temperature at which the first crystal appear, wax appearant temperature (WAT), and causes nucleation and small wax particles. The additive may come out of solution at the oil WAT and co-crystallizes with the wax, forming weak and deformed aggregates. Finally, if the additive comes out of solution at a temperature slightly lower than the oil WAT, it adsorbs on the wax crystals, inducing the dispersion of the wax crystals **[115]**. described results reported by **[164]** in which it was shown that polymer additives crystallize before the paraffins and initiate the crystallization in the form of thin pyramidal lamellae or pseudo-spherical vesicles, on which paraffin crystals agglomerate in the shape of dihedra or hollow cones, making the wax cake weaker.

Table (3.4): Pour Point Measurements for PEAA-1 (PPD) at QPC Crude.

Conc. ppm	PP (°C)				
	BS	BS10	BS15	BS20	KAR
0	39	36	36	33	30
100	39	36	36	33	27
250	39	33	33	30	27
500	39	33	30	30	27
1000	36	33	30	30	21
2000	36	30	27	30	21
5000	33	30	27	27	24
10,000	30	27	24	21	12
11,000	30	27	27	24	12

BS 10 (BS diluted with 10 % of Wady Rayan crude)
BS 15 (BS diluted with 15 % of Wady Rayan crude)
BS 20 (BS diluted with 20 % of Wady Rayan crude)

Table(3.5): Pour Point Measurements for PEAA-2 (PPD) at QPC Crude

Conc. ppm	PP (°C)				
	BS	BS10	BS15	BS20	KAR
0	39	36	36	33	30
100	39	36	36	33	30
250	39	36	36	30	27
500	36	33	33	30	27
1000	36	33	33	30	27
2000	36	33	33	30	24
5000	36	33	30	27	24
10,000	33	30	27	24	18
11,000	33	30	27	24	18

Table(3.6): Pour Point Measurements for PEAA-3 (PPD) at QPC Crude.

Conc. ppm	PP (°C)				
	BS	BS10	BS15	BS20	KAR
0	39	36	36	33	30
100	39	36	36	33	27
250	39	36	36	33	27
500	36	36	33	30	24
1000	33	33	33	30	21
2000	33	33	30	30	21
5000	33	30	30	27	15
10,000	30	27	27	21	12
11,000	27	27	24	21	12

Table(3.7): Pour Point Measurements PEAA-4 (PPD) at QPC Crude

Conc. ppm	PP (°C)				
	BS	BS10	BS15	BS20	KAR
0	39	36	36	33	30
100	36	33	33	33	30
250	36	33	33	33	30
500	36	33	30	30	27
1000	33	30	30	30	24
2000	30	30	27	27	21
5000	30	30	27	27	18
10,000	27	27	24	24	15
11,000	30	27	24	24	15

Similar observations were reported by **[40]** in a work on the crystallization of wax from distillate fuels in the presence of pour depression additives. These effects may reflect the lack or excess of polymer precipitation at the oil WAT. However, these differences may also have their origin in the polydispersity of both the polymer and the paraffin. From the preliminary results presented in this report, it may be inferred that for certain crude oils it seems possible to select an appropriate additive temperature representative of a crude oil polymer condition to assess the efficiency of paraffin deposition inhibitors. This procedure would be very useful to assess the performance of paraffin deposition inhibitors and could also be used to orient the development copolymers formulations with the potential to prevent the formation of these deposits.

3.4. EFFECT OF ADDITIVES ON PARAFFIN DEPOSITION:

The static simulator (cold finger) was used for the study of deposit formation using QPC petroleum. The results of paraffin deposit formation dependence with time are shown in **Figures (3.8- 3.13).** These results depend on the temperature variation of the hot bath, i.e., from 40 to 60 °C, and the temperature variation of the cold bath, which varies from -1 to 7 °C. Note finally that the experiments were made simultaneously in two different recipients. The plots were made through the dimensionless temperature vs.

time. The dimensionless temperature is given by the expression in equation: T – To/TH – T.

The value of To is obtained through the experimental data analysis as being the smallest value among a series of values registered from bulk fluid temperature, so, it is the smallest value of T bulk in temperature acquisition. The vessel temperature decreases due to the contact with the cold finger and when the nucleation of the petroleum starts by the same contact with the cold surface of the cold finger, the temperature suffers an inversion, beginning to increase **[107]**.

That increase of the temperature is characterized by the formation of the paraffin particles that begin to deposit on the cold finger increasing the heat transfer resistance and consequently increasing the fluid bulk temperature. The deposit only happens when the temperature difference is greater than the critical temperature difference. Then, when an inflection in the dimensionless temperature curve vs. time is found, the To wanted value is obtained, and it is the initial steady-state temperature. It corresponds to the critical time for deposit formation. In that way, a critical temperature difference between the cold fluid (inside the cold finger) and the fluid in the vessel (petroleum) must exist for the paraffin deposition to occur. As the temperature difference increases, the deposition grows more quickly. The obtained critical temperature difference for the QPC (BS) petroleum was 4.38 °C and 5.09 °C for Karama petroleum.

By using Eq. (1.11), it was possible to obtain the thickness of the formed deposit through the thermal balance between the cold finger and the hot bath. In this case, the increasing thickness is a function of the dimensionless bulk fluid temperature. The deposit thickness from QPC crude oils with a cold finger temperature of 3 °C are shown in **Figures (3.14, 3.15)**. The hydrodynamic in the fluid can present two different effects in the formation of the paraffin deposit:

(i) Stronger impacts of particles in the paraffin deposit can increase the growth of that deposit, due to cohesion forces.

(ii) Rapidly streaming of the fluid can remove the particles not firmly stuck to the superficial layer of the deposit.

The obtained critical temperature differences for the two different petroleum crude oils used in the experiments are coherent with their nature. For the lower wax petroleum , a less critical temperature difference was obtained (4.38 °C) and for the higher wax content petroleum (BS) a higher critical temperature difference was observed (5.09 °C). The same is also observed for the paraffin deposit thickness, where the more paraffinic petroleum (BS) exhibits a more thick deposit, as shown in **Figures (3.14, 3.15)**. These values of critical temperature differences are relatively small and show that the encrustation is easily attained in the petroleum flow. From the previous study of the paraffin deposition of crude oil we can concluded that, the formation of paraffin deposits through the cold finger methodology based on

Ny′ vlt's development for the deposition from binary mixtures was studied **[97]**.

The use of Ny′ vlt's **[97]** methodology together with dimensional group analysis coupled with a simple cold finger apparatus allows us to quantify the tendency of paraffin deposition in cooling petroleum flow. The critical temperature difference is a function of the complex establishment of the supersaturation of the paraffin in petroleum solution due to temperature difference between the two sources (heat and cold). This methodology allows us to find this critical temperature difference. If the nucleation of paraffin is conducted in the petroleum bulk, with temperature difference less than the critical temperature difference, no deposit will be observed. Concluding, if there was the existence of paraffins at low supersaturation in the petroleum bulk, no nucleation will happen at the cold surface inhibiting the deposit formation. If the critical temperature difference is attended, nucleation will occur at the pipe wall surface and the growth of this layer will cause an increase of the deposit and the necessity of cleaning this surface, causing a production loss. The same can be said with relation to the critical time.

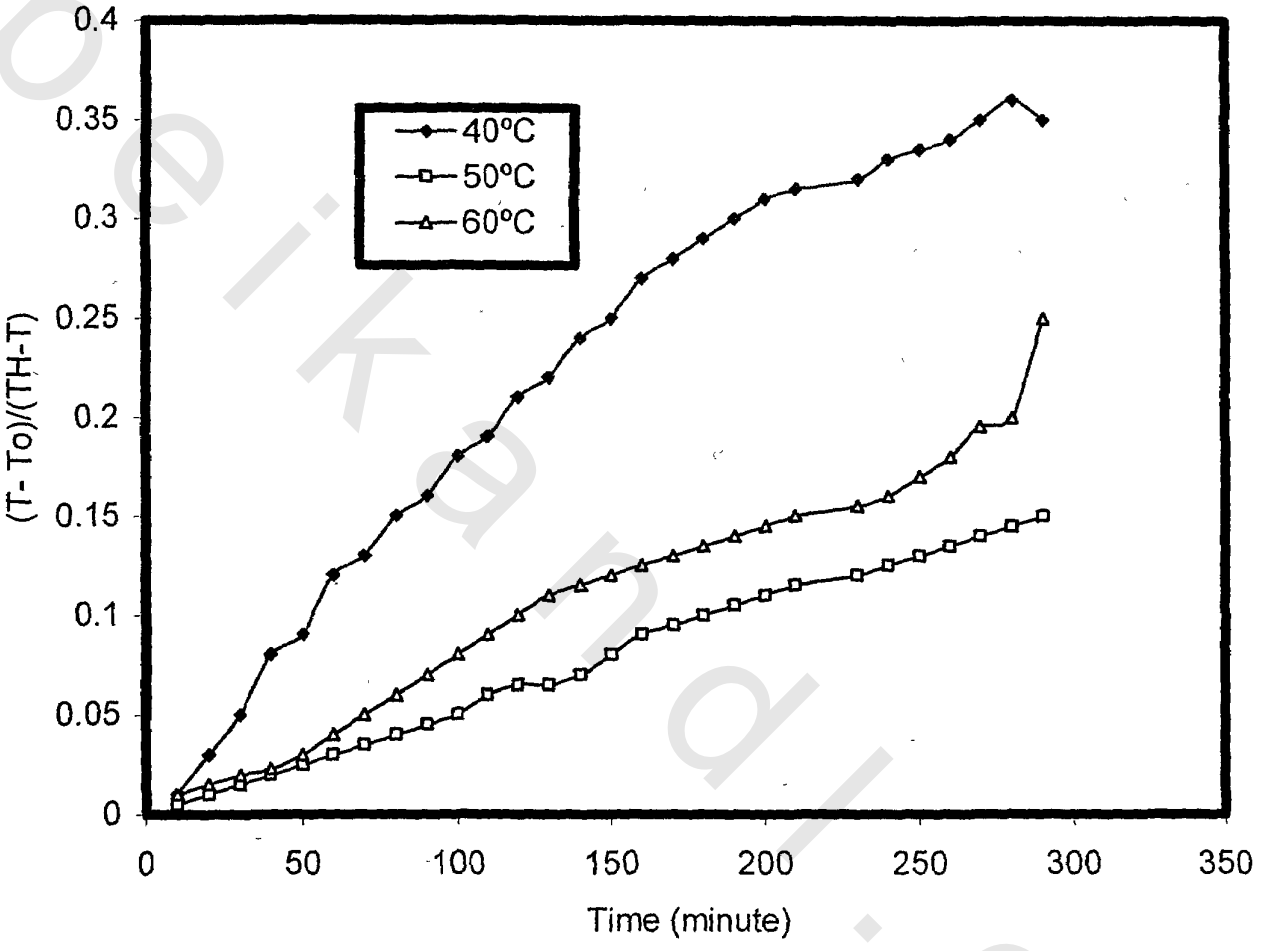


Figure (3.8). Dependence of vessel 1 temperature with deposit thickness along time, using KARAMA petroleum with hot bath temperature at 40, 50 and 60 °C and cold finger temperature at -1 °C.

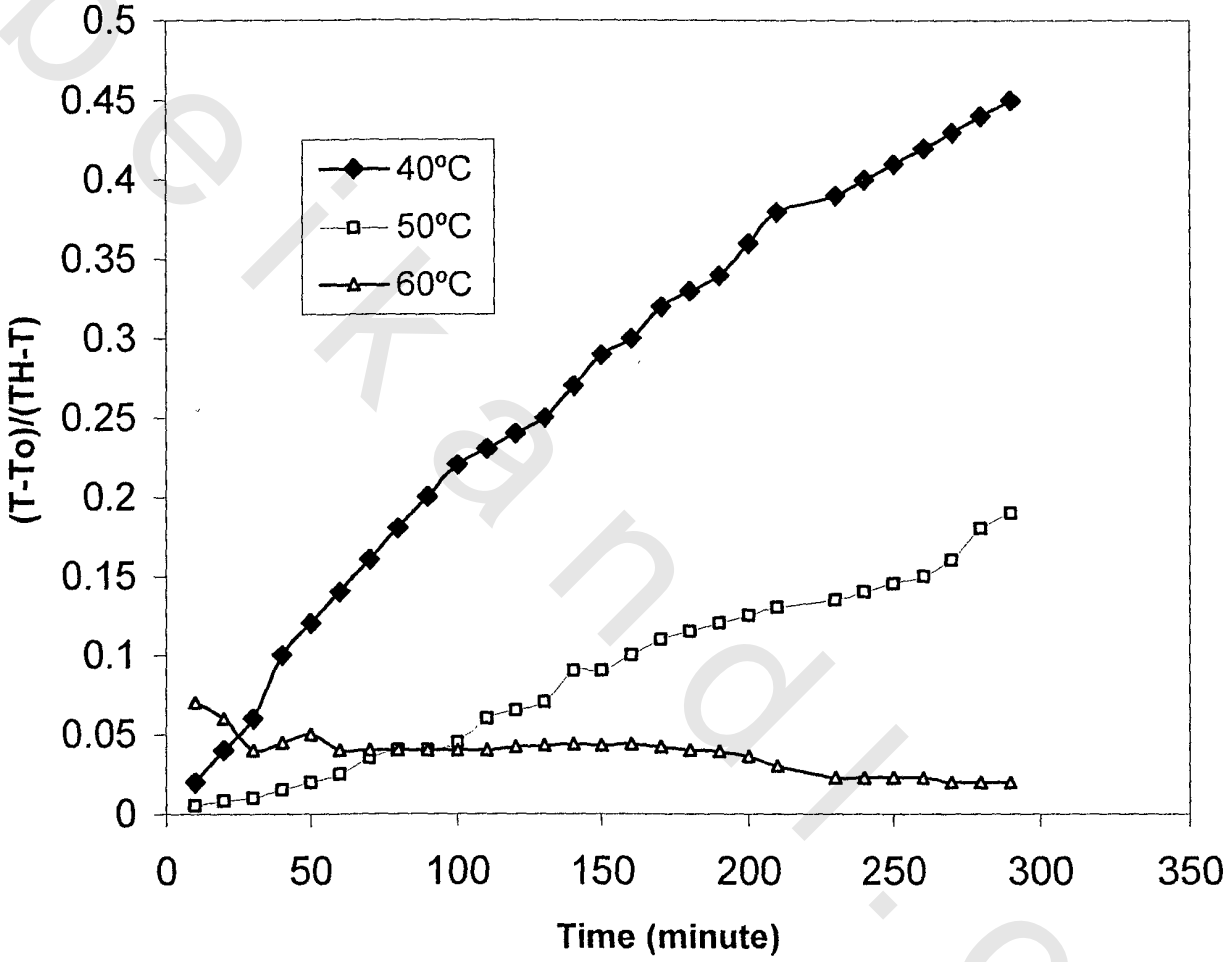


Figure (3.9). Dependence of vessel 1 temperature with deposit thickness along time, using KARAMA petroleum with hot bath temperature at 40, 50 and 60 °C and cold finger temperature at 3 °C.

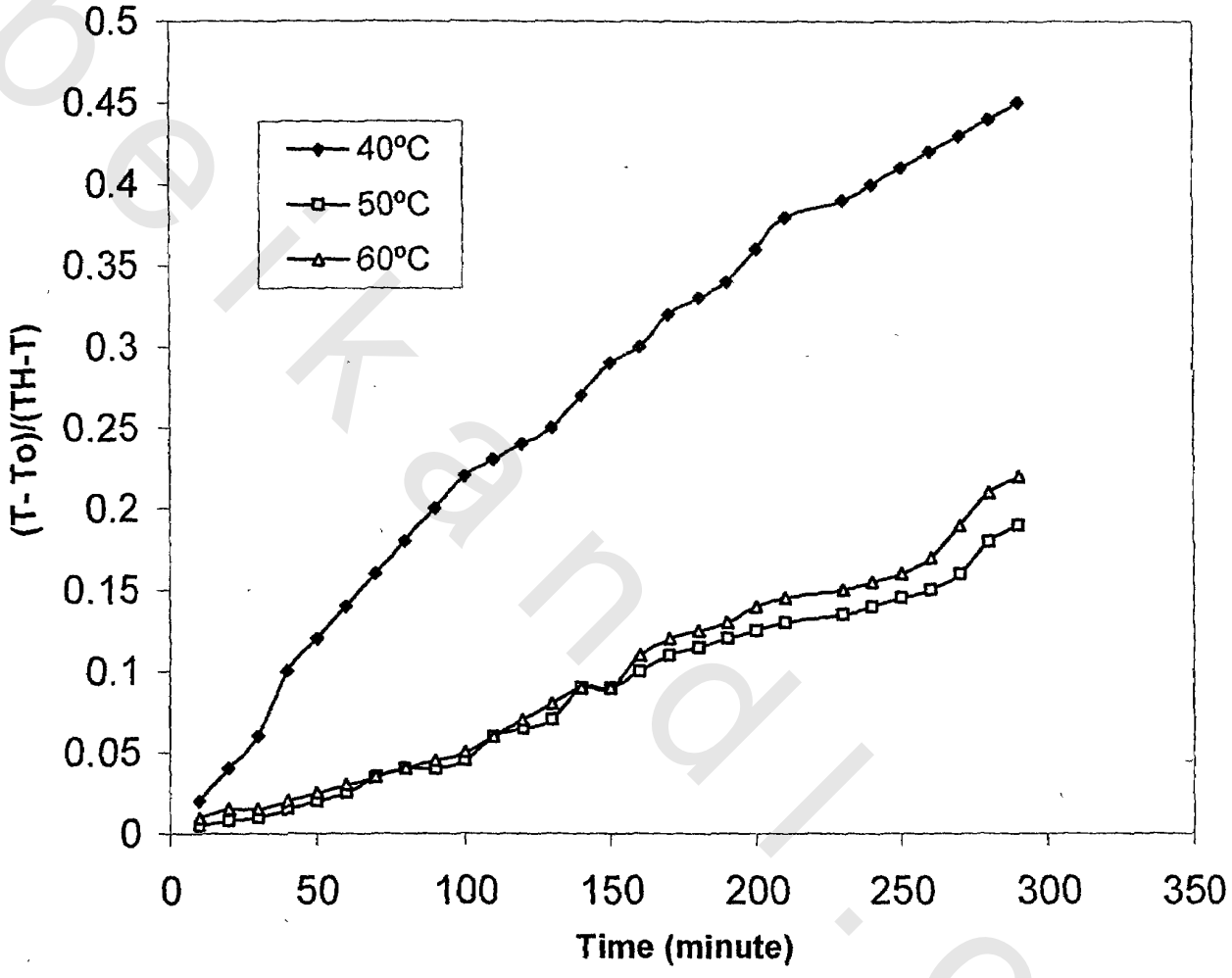


Figure (3.10). Dependence of vessel 1 temperature with deposit thickness along time, using KARAMA petroleum with hot bath temperature at 40, 50 and 60 °C and cold finger temperature at 7 °C.

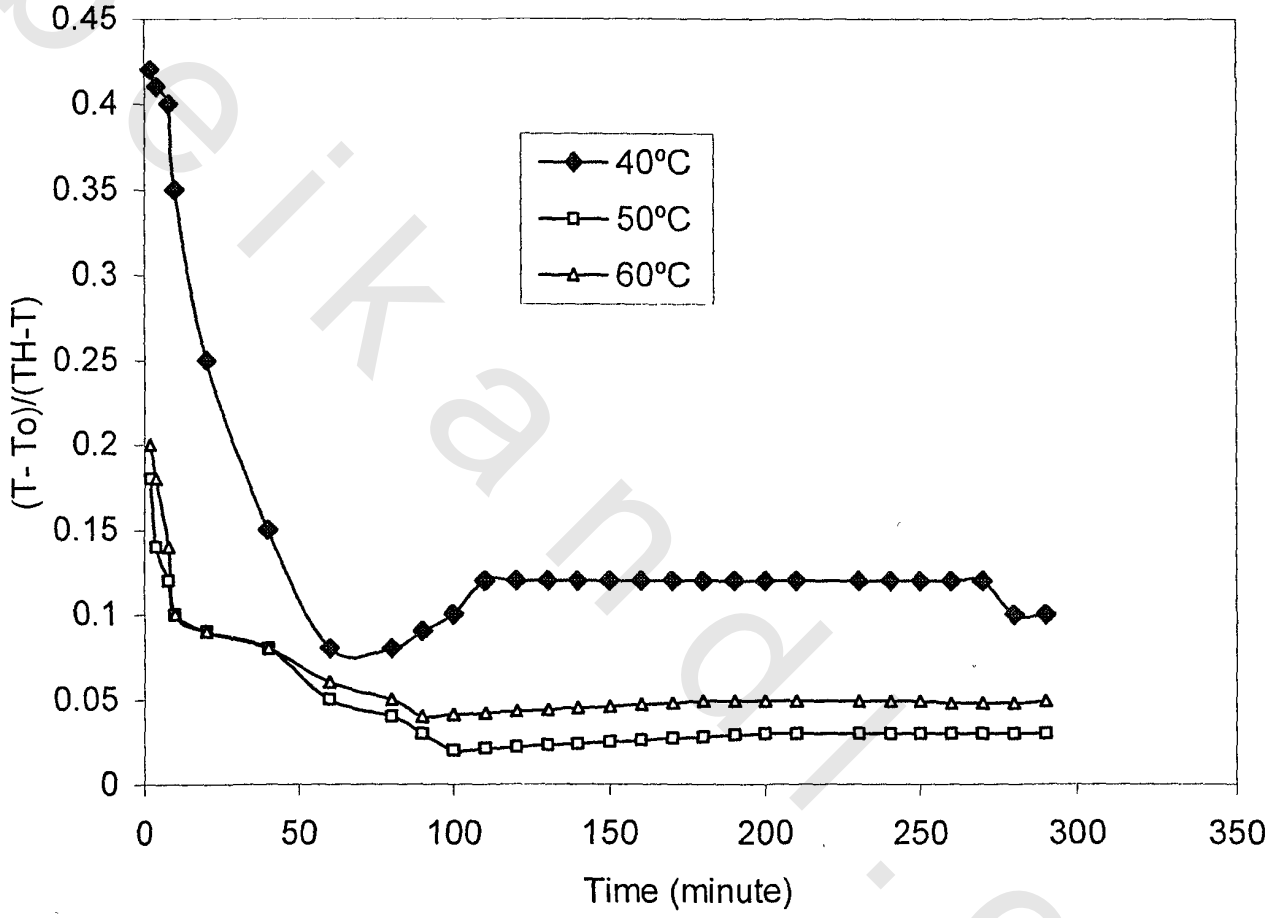


Figure (3.11). Dependence of vessel 1 temperature with deposit thickness along time, using BS+20%WR petroleum with hot bath temperature at 40, 50 and 60 °C and cold finger temperature at -1°C.

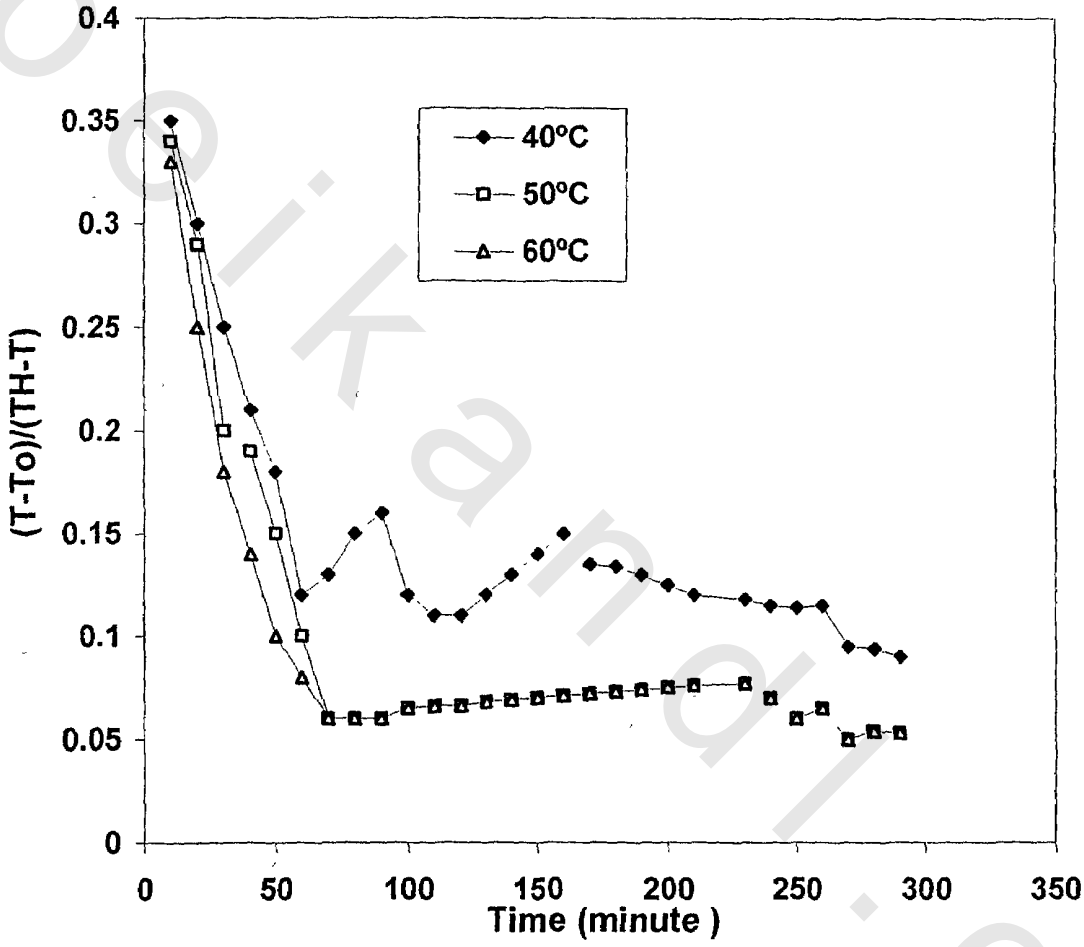


Figure (3.12). Dependence of vessel 1 temperature with deposit thickness along time, using BS+20%WR petroleum with hot bath temperature at 40, 50 and 60 °C and cold finger temperature at 3°C.

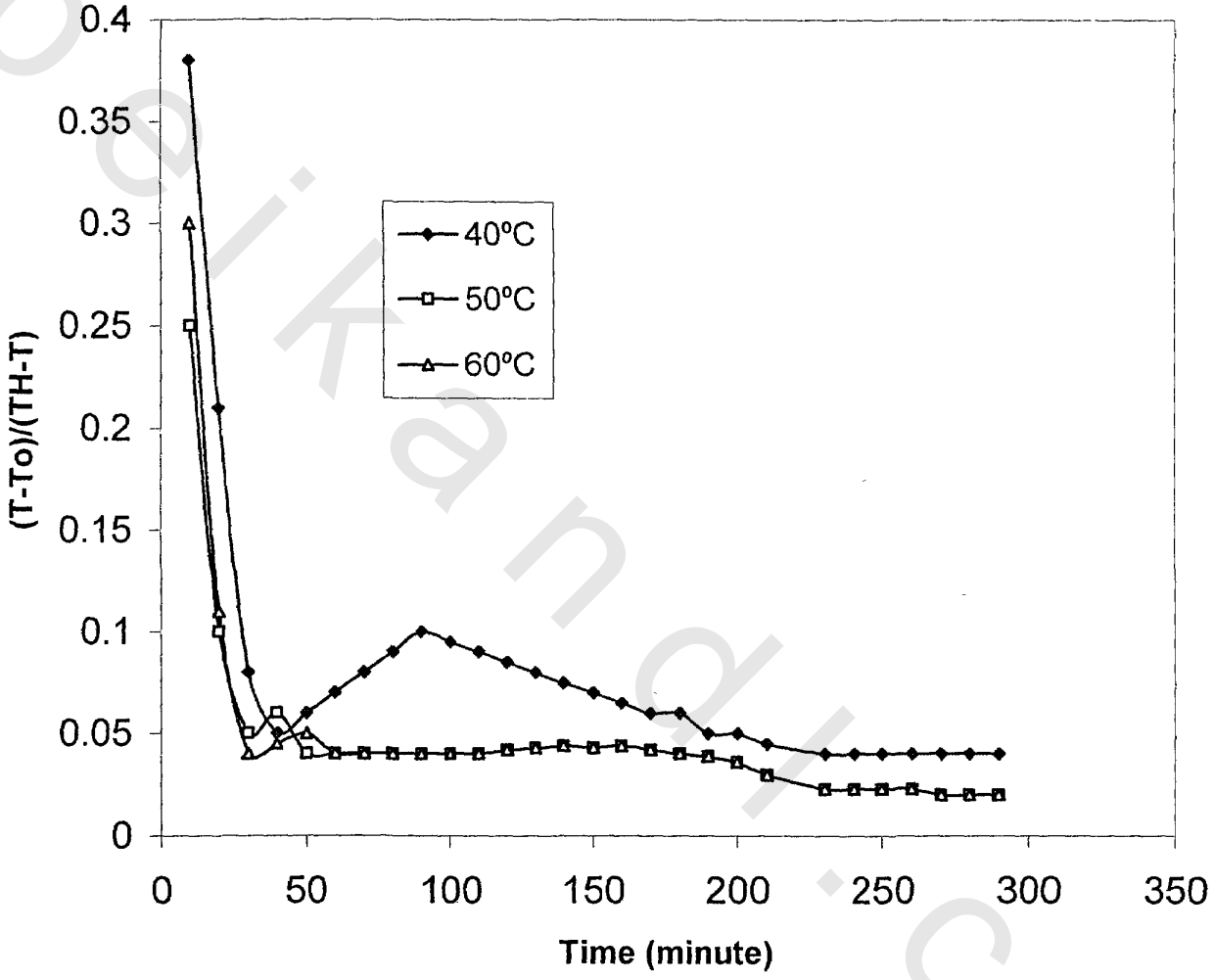


Figure (3.13). Dependence of vessel 1 temperature with deposit thickness along time, using BS+20%WR petroleum with hot bath temperature at 40, 50 and 60 °C and cold finger temperature at 7°C.

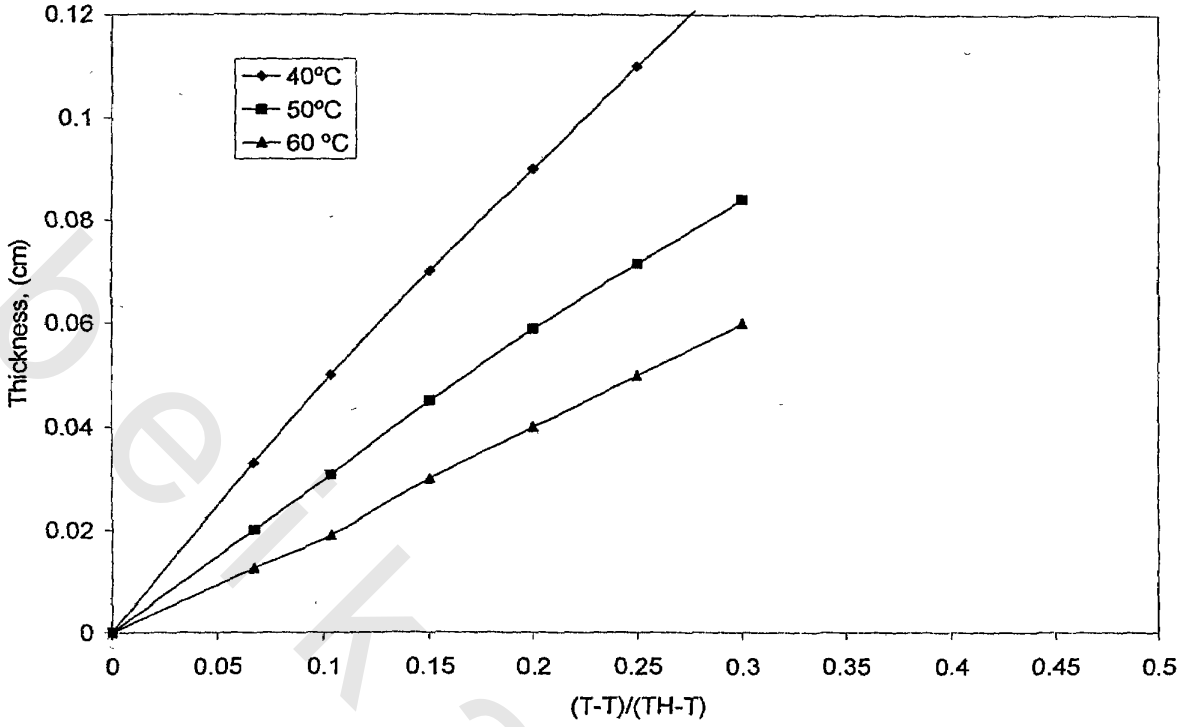


Figure (3.14): Deposit thickness formed for of KARAMA petroleum with cold finger temperature at 3 °C in vessel 1.

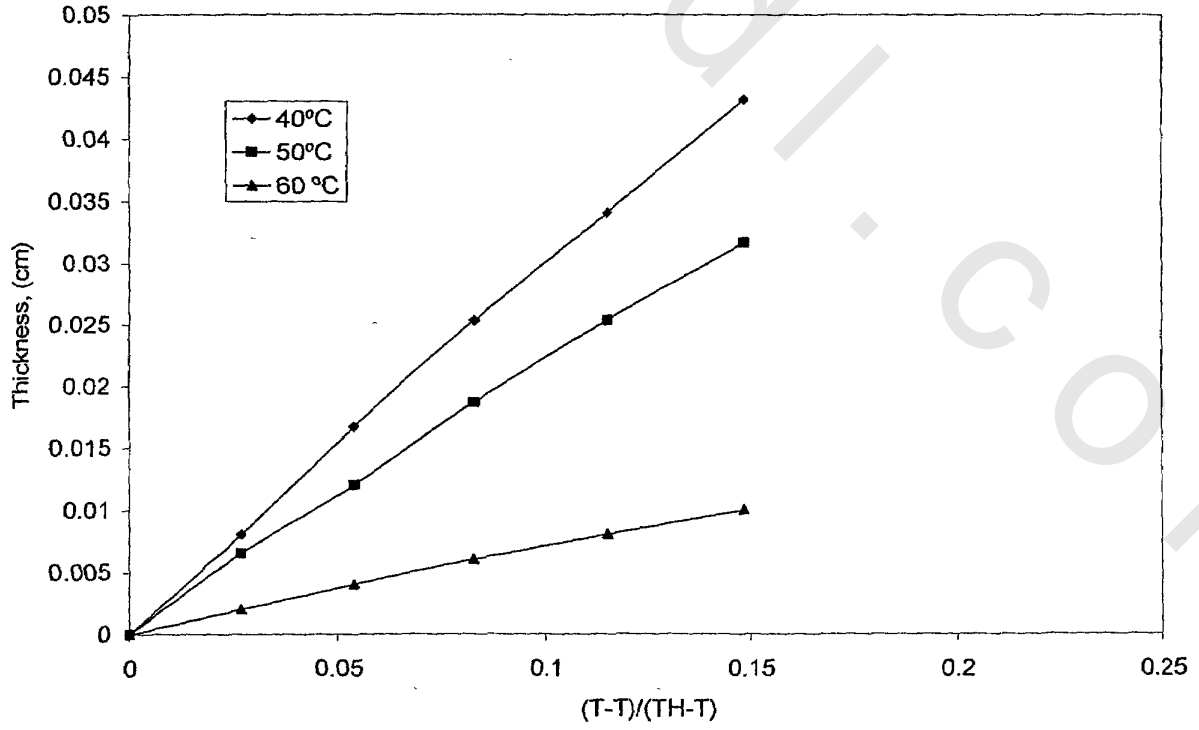


Figure (3.15): Deposit thickness formed for of BS/20 %WR petroleum with cold finger temperature at 3 °C in vessel 1.

In this way, two possible mechanisms are possible, depending on how the supersaturation is attained:

(i) If the critical temperature is attained at the surface, nucleation will occur at the pipe wall surface and with the crystalline growth, a deposit will be formed and a production loss will happen.

(ii) If the temperature difference between the pipe wall and the petroleum bulk will be established less than the critical temperature difference, nucleation will occur at the petroleum bulk and no deposit by incrustation will occur and no losses in production will happen.

The methodology implemented in this work is simple and allows the prediction of very important information about the mechanism of paraffin encrustation, for example, the critical temperature difference. This methodology that was developed for industrial crystallization, mainly for inorganic chemicals, was successfully applied here for the petroleum industry. This kind of information could pave the way to avoid the paraffin deposition in offshore petroleum production due to high temperatures differences between the heat petroleum sink source and the cold seawater. Implementing good apparatus to attenuate this temperature difference can improve production rates, for example, with new insulating riser pipes or double pipe risers.

1. The greater the temperature difference between the oil and the wall, the greater the deposition rate.

2. The initial temperature of the oil does not significantly alter the deposition rate.

3. The deposition rate decreases with increasing flow rate rather than increasing as indicated by present deposition simulation tools.

4. The oil content of the deposits in turbulent flow was significantly lower than the oil content of the deposits in laminar flow.

In the present work, the deposition of wax with cold finger by two methods which are based on thickness and mass of deposit. Laboratory experiments until recently were conducted using a Cold Finger Apparatus. A schematic diagram of the Cold Finger Apparatus is shown in **Figure (2.1)**. The Cold Finger Apparatus is suitable only to measure the total mass of the deposit at the end of the experiment. In this respect, the measured mass and thickness of deposit for tested crude oil BS diluted with 20% of Wady Rayan and Karama crude oil in absence and presence of PEAA blend with HRA were listed in **Tables (3.8 – 3.11).** It was noted that the additives produce soft wax while the crude without additive have hard deposit. However, it is more desirable to have the soft deposit in the system because they are easily removed by pigging or can even be continuously removed by shear of the oil production. The data indicate that the additives were more efficient in reducing the deposition thickness and mass of the oil obtained from the BS and Karama field. For the Benisuif field, the

additives presented the following performance order: PEAA-2 < PEAA-4 < PEAA-1< PEAA-3. PEAA-3 achieves the best performance as paraffin dispersant at the same concentration of other additives. So the same discussion in the last section of pour point will be reported in the case of wax deposition.

The deposition rate cannot be measured. Furthermore, it uses only a small volume of crude to conduct an experiment that could lead to misleading results. The observed deposition behavior using this apparatus is not entirely field-like and there is reason to question the field applicability of the results **[160]**. Because the Cold Finger Apparatus suffers from these drawbacks, a setup that would simulate the deposition in wells was formulated.

3.5. EFFECT OF ADDITIVES ON RHEOLOGY OF CRUDE OILS

The rheological behavior of a crude oil is highly influenced by its chemical composition, temperature and the current, as well as previous thermal history. High waxy crudes exhibit a non-Newtonian character, often with a yield shear stress at and below their pour point temperature. At a sufficiently high temperature of the crude oil, although chemically very complex, is a simple Newtonian liquid. If the waxy crude oil is allowed to cool, wax will crystallize, agglomerate and entrap the oil into its structure.

Table(3.8): Cold Finger Measurements PEAA-1 using QPC Crude.

Conc. ppm	Total wax deposited (g)									
	BS	Red.* (%)	BS10	Red.* (%)	BS15	Red.* (%)	BS20	Red.* (%)	KAR	Red.* (%)
0	40	0	35	0	32	0	30	0	35	0
100	40	0	35	0	32	0	30	0	33	5.7
250	40	0	35	0	32	0	30	0	30	14.3
500	40	0	26	25.71	32	0	24	20	26	25.71
1000	30	25	26	25.71	24	25	23	23	26	25.71
2000	25	37.5	26	25.71	22	31.25	18	40	24	31.43
5000	22	45	20	42.86	18	43.75	15	50	17	51.42
10000	18	55	16	54.3	15	53.12	12	60	11	68.57

- **Percent reduction**
- **All these experiments were done with oil temperature 40 ^{o}C and a wall temperature of 7^{o}C for 5h.**

Table(3.9): Cold Finger Measurements PEAA-2 using QPC Crude .

Conc. ppm	Total wax deposited (g)									
	BS	Red.* (%)	BS10	Red.* (%)	BS15	Red.* (%)	BS20	Red.* (%)	KAR	Red.* (%)
0	40	0	35	0	32	0	30	0	35	0
100	40	0	35	0	32	0	30	0	33	5.7
250	40	0	35	0	32	0	30	0	32	8.6
500	40	0	30	14.2	32	0	27	10	30	14.3
1000	35	12.5	30	14.2	30	6.25	27	10	30	14.3
2000	30	25	30	14.2	28	12.5	24	20	28	20
5000	25	37.5	25	28.6	24	25	20	33	22	37
10,000	22	45	23	35	20	37.5	18	40	15	57.14

- **Percent reduction**
- **All these experiments were done with oil temperature 40 ^{o}C and a wall temperature of 7^{o}C for 5h.**

Table(3.10): Cold Finger Measurements PEAA-3 using QPC Crude .

Conc. ppm	Total wax deposited (g)									
	BS	Red.* (%)	BS10	Red.* (%)	BS15	Red.* (%)	BS20	Red.* (%)	KAR	Red.* (%)
0	40	0	35	0	32	0	30	0	35	0
100	40	0	35	0	32	0	30	0	33	5.7
250	40	0	35	0	32	0	30	0	30	14.3
500	40	0	24	31.5	32	0	24	20	24	31.4
1000	28	30	24	31.5	20	37.5	20	33	24	31.4
2000	25	37.5	20	43	20	37.5	15	50	22	37.1
5000	22	45	15	57	13	54.3	10	67	15	57
10,000	14	65	12	65.7	8	68.6	5	83.3	8	77.1

- **Percent reduction**
- **All these experiments were done with oil temperature 40 ^{o}C and a wall temperature of 7^{o}C for 5h.**

Table(3.11): Cold Finger Measurements PEAA-4 using QPC Crude .

Conc. ppm	Total wax deposited (g)									
	BS	Red.* (%)	BS10	Red.* (%)	BS15	Red.* (%)	BS20	Red.* (%)	KAR	Red.* (%)
0	40	0	35	0	32	0	30	0	35	0
100	40	0	35	0	32	0	30	0	33	6
250	40	0	35	0	32	0	30	0	31	11.5
500	40	0	28	20	32	0	26	14	28	20
1000	33	17.5	28	20	26	19	25	17	28	20
2000	28	30	28	20	24	25	23	23	26	26
5000	25	37.5	22	37	20	38	18	40	20	43
10,000	20	50	18	48.5	16	50	15	50	13	63

- **Percent reduction**
- **All these experiments were done with oil temperature 40 ^{o}C and a wall temperature of 7^{o}C for 5h.**

This phenomena often happens if the ambient temperature of the place is below the pour point of the crude oil. Pretreatment of the crude oil is necessary for transportation of these waxy crudes through the pipeline. Pretreatment of the crude oil with flow improver is one method by which the rheological character of the gelled waxy crude is changed for easier transportation Flow improver additive, alternatively known as pour point depressant (PPD)/wax crystal modifier, can reduce the growth of the wax crystal and forms smaller crystals of a higher volume to surface ratio. Owing to this change in crystal shape the ability of wax crystals to intergrow and interlock is greatly diminished. The combination of these two effects lowers the pour point, viscosity and yield shear stress appreciably, and it becomes easier for the transportation of waxy crude oil. But wax is not the only component in a crude oil. Other constituents in the crude oil i.e. asphaltenes, resins, lighter distillates, polar aromatics etc. should also be considered as important factors while ascertaining the flow behavior of a crude oil. Asphaltenes are very large heterogeneous molecules with condensed aromatic nuclei, which may associate to form colloidal sized particles that strongly influence the viscosity of the oil medium and affect the crystallization of the wax. A number of polymeric compounds such as poly alkylacrylates and methacrylate copolymers, alkyl esters of styrene-maleic anhydride copolymers, alkyl acrylate, ethylene-

vinyl acetate copolymers, alkyl fumarate-vinyl acetate copolymers are some of the FI/PPD for waxy crude oil.

3.5.1. Rheological Behavior of the Systems: Crude Oil and Crude oil/PEAA Copolymer

To assure a realistic low temperature flow behavior of the tested crude oils, rheological measurements have to be evaluated. Data obtained from pour point and wax deposition tests revealed that, the prepared PEAA grafts have different dispersant capabilities for all tested crude oils. Hence, these additives were evaluated for their performance as flow improvers in the three tested crude oils through rheological measurements at concentration of 100, 250, 500, 1000, 2000, 5000 and 10,000 ppm. Measurements of the shear stress – shear rate relationship were carried out at different temperatures ranging from 48 °C to 15 °C. The experimental procedure starts with doping the crude with the additive at the prescribed concentration at 65 °C; meanwhile, the viscometer cup is preheated to the same temperature, then loaded with 25 ml of the heated sample, and the temperature is brought down at the test temperatures 48 °C, 35 °C and 15 °C at a low shear rate of 7.29 S^{-1} (dynamic cooling). Shearing was continued for 15 min at the test temperature before evaluation. The shear stress- shear rate relationship was recorded for the tested samples. Experimental data were fitted to Bingham plastic flow model using a linear

regression computer program. The Bingham plastic flow model is represented by the equation:

$$\tau = \tau_y + \eta_p \frac{du}{dr} \quad (3.1)$$

Where τ is the shear stress (Pascal; pa); τ_y is the yield shear stress (pa); η_p, the plastic viscosity (milli- Pascal second; m Pa. S); and **du/dr** is shear rate (S^{-1}).

The rheological behavior of crude oil is highly influenced by its chemical composition, temperature as well as thermal history. High waxy crude oils exhibit a non-Newtonian character, often with a yield shear stress at and below their pour point temperature. The effect of wax content on the rheological behavior of highly wax crude oils, is well be tended in this section. In this respect, BS, BS blend with 20% of WR and KARAMA crude oils were selected on the basis of varied wax content (16-21%). The data of shear stress-shear rate relationships of crude without treatments, listed in **Table (3.12)**, show that the plastic viscosity (mPaS) and yield shear stress values (Pa) increased with increasing wax contents. All crude oils show non-Newtonian character even at high temperatures 45 °C. This indicates that the wax affects the rheological behaviors of the crude oils. The data listed in **Table (3.12)** indicate that the tested crude oils possess high yield shear stress values at low temperature at and blew their pour points. On the other hand, it was observed that the viscosity of crude oils was increased with cooling. It is well known that, the crude oil

components (such as wax, asphaltenes, resins, lighter distillates, polar aromatic, etc.) should be considered as important factors while ascertaining the flow behavior of a crude oil. Therefore, the high wax content leads to the formation of gelled crude at low temperatures due to the crystallization of the wax and that will affects the viscosity of crude oils.

3.5.2. Influence of PEAA Grafts on Rheology of Treated Crude Oils:

The shear stress – shear rate relationships for the untreated and treated crude oils with PEAA-4 at different concentrations and temperatures 36 and 15 °C were not represented here for brevity. These figures illustrate the fitted experimental data of both shear stress and shear rate measurements according to the Bingham plastic model. The obtained data of η_p, τ_y and correlation coefficient were determined for all tested crude oils at different temperatures and listed in **Tables (3.13- 3.21)**. The manner by which a fluid obeys a given shear stress- shear rate relationship determines its class within the rheological classification of a fluid. A fluid is said to be Newtonian when it obeys Newtonian's law of viscosity, given by the equation:

$$\tau = \eta_p \frac{du}{dr} \qquad (3.2)$$

So, a Newtonian fluid is one whose viscosity at a given temperature is independent of the shear rate. The viscosity of a

Newtonian fluid at a given temperature is constant regardless of the viscosity, previous agitation or shearing of the fluid. For a Newtonian fluid, a linear plot of log τ versus log du/dr gives a straight line with a slop of unity. Both types of plots are useful in characterizing a Newtonian fluid. For a Newtonian fluid, the viscosity may be a function of temperature, pressure and crude oil composition. Moreover, the viscosity of a Newtonian fluid is not a function of the duration neither of shear nor of time laps between consecutive applications of shear rate. The effect of structure and concentration of these polymers on rheological characteristics, such as viscosity and yield shear stress values, of QPC crude oils will be evaluated. The data of plastic viscosity and yield shear stress values were determined for all treated crude oils with PEAA grafts and tabulated in **Tables (3.13-3.21)**. On the other hand, the apparent viscosities (mPa.S) of the untreated and treated crude oils with PEAA-4 grafts were determined at different temperatures to evaluate the effect of the polymer on the viscosities of BS crude and the results are shown as representative samples in **Figures (3.16-3.18)**. The data indicate that the viscometric behaviors of the treated crude oils depend on the crude oil compositions and the structure of the prepared PEAA copolymeric additives. In this respect, the values of the plastic viscosity (mPa.S) and yield shear stress values (Pa) decreased by the addition of PEAA additives even at high concentrations (10,000 ppm). The results listed in **Tables (3.13-3.21)** indicate that the reduction in values of both

viscosity and yield shear stress were strongly depended on the type of the copolymer used. PEAA-2 has a reduced efficiency at higher concentrations whereas PEAA-3, which presents a poor performance at low concentrations, becomes better in more concentrated solutions. PEAA- 2 achieves the best performance as lower viscosity values at a lower concentration.

This means that, in this concentration range, the additive cocrystallizes with the paraffin, modifying their crystals. The loss of efficiency observed at higher concentration may be ascribed to precipitation of the pure copolymer, or to wax crystallization with nucleation induced by the copolymer.

Nonetheless, it is interesting to note that in this concentration range, PEAA-3 also loses its efficiency as viscosity reducer. PEAA-1 and PEAA-4 exhibited a similar behavior, that is, they presented an optimum performance concentration at a concentration higher than PEAA-3, but they maintained their capacity to reduce the crude pour point at higher concentrations. By comparing PEAA-1 and PEAA-4, the minimum concentration to achieve the best performance is slightly higher for the PEAA-4 than that for the PEAA-1. At the concentration range tested, PEAA-2 was not able to reduce the crude oil pour point, even through the rheological study showed that PEAA-2 can reduce the crude oil viscosity. In order to explain this apparent disagreement between viscosity and pour point behavior it is necessary to consider the physical situation prevailing in each test separately.

Table (3.12): Rheological Data of Untreated Different Crude Oils at Different Temperatures.

Crude Oils	Tests	Temperatures		
		15 °C	36 °C	48 °C
BS	Yield stress value Pa*	142.6	100.2	8.85
	Plastic viscosity mPa.S**	234.7	175.3	145.7
	Correlation coefficient	0.9991	0.9961	0.9991
BS +20%WR	Yield stress value Pa	98.45	85.24	6.45
	Plastic viscosity mPa.S	190.17	134.62	95.4
	Correlation coefficient	1.0	1.0	1.0
KARAMA	Yield stress value Pa	76.9	60.85	4.45
	Plastic viscosity mPa.S	92.34	79.5	54.8
	Correlation coefficient	0.9996	0.9959	0.9993

*where: Pa, Pascal

**where: mPa S, milli- Pascal second

Table (3.14): Rheological Data of BS Crude Oil with PEAA Grafts at 48 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of BS Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	8.85	154.7	0.9991
PEAA-1	100	4.92	44.6	0.9996
	250	4.52	40.8	0.9993
	500	3.91	32.87	0.9982
	1000	3.503	30.78	0.9965
	2000	2.196	28.67	0.9994
	5000	0.0084	27.32	0.9996
	10000	0.0005	26.32	0.9993
PEAA-2	100	5.453	34.6	0.9982
	250	4.334	30.8	0.9965
	500	4.231	29.87	0.9994
	1000	3.342	28.78	0.9996
	2000	2.102	27.67	0.9993
	5000	1.674	24.32	0.9982
	10000	1.543	13.32	0.9965
PEAA-3	100	2.342	54.6	0.9994
	250	2.321	50.8	0.9996
	500	2.064	40.87	0.9993
	1000	1.123	35.78	0.9982
	2000	0.987	30.67	0.9952
	5000	0.00986	14.32	0.9994
	10000	0.00134	13.32	0.9996
PEAA-4	100	3.341	38.6	0.9993
	250	3.211	32.8	0.9982
	500	2.8975	31.87	0.9965
	1000	2.231	30.78	0.9994
	2000	1.0987	29.67	0.9996
	5000	0.675	21.32	0.9993
	10000	0.0053	20.32	0.9982

Table (3.14): Rheological Data of BS Crude Oil with PEAA Grafts at 36 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of BS Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	100.2	175.3	0.9961
PEAA-1	100	15.9192	78.942	1.0
	250	15.2443	65.867	1.0
	500	15.032	58.572	1.0
	1000	14.441	49.781	1.0
	2000	13.3903	29.839	1.0
	5000	12.2805	25.561	1.0
	10000	2.013	19.823	1.0
PEAA-2	100	27.9192	48.942	1.0
	250	25.2443	44.867	1.0
	500	21.452	39.572	1.0
	1000	20.4889	35.781	1.0
	2000	1 9.3903	34.839	1.0
	5000	1 8.2805	32.561	1.0
	10000	1 7.8285	25.823	1.0
PEAA-3	100	18.9192	78.942	1.0
	250	1 8.2443	64.867	1.0
	500	17.452	58.572	1.0
	1000	16.4889	29.781	1.0
	2000	14.3903	24.839	1.0
	5000	1.0025	18.561	1.0
	10000	0.056	17.823	1.0
PEAA-4	100	17.9192	58.942	1.0
	250	17.2443	53.867	1.0
	500	16.452	48.572	1.0
	1000	1 5.4889	39.781	1.0
	2000	1 4.3903	34.839	1.0
	5000	1 0.02805	27.561	1.0
	10000	1 0.08285	24.823	1.0

Table (3.15): Rheological Data of BS Crude Oil with PEAA Grafts at 15 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of BS Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	142.6	234.7	0.9991
PEAA-1	100	28.7346	95.706	1.0
	250	2 6.7063	81.286	1.0
	500	25.1088	76.478	1.0
	1000	24.7015	69.93	1.0
	2000	17.2883	50.185	1.0
	5000	4.1662	44.978	1.0
	10000	0.045	29.17	1.0
PEAA-2	100	5 8.7346	115.706	1.0
	250	4 6.7063	61.286	1.0
	500	3 7.1088	56.478	1.0
	1000	36.7015	47.93	1.0
	2000	27.2883	40.185	1.0
	5000	10.1662	34.978	1.0
	10000	8.7344	29.77	1.0
PEAA-3	100	48.5346	125.306	1.0
	250	43.2063	111.286	1.0
	500	37.8088	106.478	1.0
	1000	30.6015	99.93	1.0
	2000	21.4883	80.185	1.0
	5000	2.3662	40.978	1.0
	10000	0.0324	25.17	1.0
PEAA-4	100	38.7346	115.706	1.0
	250	36.7063	91.286	1.0
	500	34.1088	86.478	1.0
	1000	33.7015	77.93	1.0
	2000	27.2883	70.185	1.0
	5000	16.1662	54.978	1.0
	10000	4.7344	49.77	1.0

Table (3.16): Rheological Data of Treated BS+20%WR Crude Oil with PEAA Grafts at 48 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of BS+20%WR Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	6.45	95.4	1.0
PEAA-1	100	3.42	24.6	1.0
	250	3.12	20.8	1.0
	500	2.98	12.87	1.0
	1000	2.103	10.78	1.0
	2000	1.896	8.67	1.0
	5000	0.0054	7.321	1.0
	10000	0.0003	6.321	1.0
PEAA-2	100	4.453	14.6	1.0
	250	2.334	10.8	1.0
	500	2.031	9.87	1.0
	1000	1.3421	8.78	1.0
	2000	1.102	7.67	1.0
	5000	0.674	5.321	1.0
	10000	0.543	4.321	1.0
PEAA-3	100	1.342	34.6	0.9996
	250	1.321	30.8	0.9993
	500	1.064	20.87	0.9982
	1000	1.023	15.78	0.9965
	2000	0.9876	10.67	0.99943
	5000	0.00786	4.321	0.99985
	10000	0.00034	3.321	0.99988
PEAA-4	100	2.341	18.6	0.9988
	250	2.211	22.8	0.99978
	500	1.8975	15.87	0.99991
	1000	1.231	12.78	0.99967
	2000	0.9876	10.67	0.99987
	5000	0.675	9.321	0.9999
	10000	0.0043	8.321	0.9999

Table (3.17): Rheological Data of Treated BS+20%WR Crude Oil with PEAA Grafts at 36 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of BS+20%WR Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	85.24	134.62	1.0
PEAA-1	100	15.9192	65.942	1.0
	250	15.2443	50.867	1.0
	500	14.452	44.572	1.0
	1000	11.4889	37.781	1.0
	2000	3.3903	18.839	1.0
	5000	2.2805	10.561	1.0
	10000	0.00	8.823	1.0
PEAA-2	100	17.9192	35.942	1.0
	250	15.2443	30.867	1.0
	500	11.452	24.572	1.0
	1000	10.4889	21.781	1.0
	2000	9.3903	19.839	1.0
	5000	8.2805	14.561	1.0
	10000	5.8285	5.823	1.0
PEAA-3	100	8.9192	65.942	1.0
	250	8.2443	50.867	1.0
	500	7.452	44.572	1.0
	1000	6.4889	37.781	1.0
	2000	4.3903	30.839	1.0
	5000	0.0025	5.561	1.0
	10000	0.0	4.823	1.0
PEAA-4	100	7.9192	45.942	1.0
	250	7.2443	40.867	1.0
	500	6.452	34.572	1.0
	1000	5.4889	27.781	1.0
	2000	3.3903	20.839	1.0
	5000	0.02805	14.561	1.0
	10000	0.00285	10.823	1.0

Table (3.18): Rheological Data of Treated BS+20%WR Crude Oil with PEAA Grafts at 15 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of BS+20%WR Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	98.45	190.17	1.0
PEAA-1	100	28.7346	65.706	1.0
	250	2 6.7063	51.286	1.0
	500	24.1088	46.478	1.0
	1000	20.7015	39.93	1.0
	2000	17.2883	20.185	1.0
	5000	3.1662	14.978	1.0
	10000	0.005	9.17	1.0
PEAA-2	100	4 8.7346	45.706	0.9996
	250	3 0.7063	31.286	0.9993
	500	2 1.1088	26.478	0.9982
	1000	19.7015	17.93	0.9965
	2000	17.2883	14.185	0.99943
	5000	9.1662	8.978	0.99985
	10000	6.7344	6.77	0.99988
PEAA-3	100	38.5346	95.306	0.9988
	250	33.2063	81.286	0.99978
	500	27.8088	76.478	0.99991
	1000	20.6015	69.93	0.99967
	2000	11.4883	50.185	0.99987
	5000	1.3662	10.978	0.9999
	10000	0.0009	5.17	0.9999
PEAA-4	100	28.7346	85.706	1.0
	250	26.7063	61.286	1.0
	500	24.1088	56.478	1.0
	1000	23.7015	47.93	1.0
	2000	17.2883	40.185	1.0
	5000	6.1662	24.978	1.0
	10000	4.7344	19.77	1.0

Table (3.19): Rheological Data of KARAMA Crude Oil with PEAA Grafts at 48 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of KARAMA Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	4.45	54.8	0.9993
PEAA-1	100	3.323	14.6	0.9996
	250	3.112	10.8	0.9993
	500	2.786	9.87	0.9982
	1000	2.678	5.78	0.9965
	2000	2.341	3.67	0.99943
	5000	0.075	3.321	0.99985
	10000	0.00342	2.321	0.99988
PEAA-2	100	2.453	4.6	0.9988
	250	2.213	3.8	0.99978
	500	2.043	2.87	0.9996
	1000	1.8975	1.78	0.9993
	2000	1.564	1.67	0.9982
	5000	1.453	1.321	0.9965
	10000	1.198	0.321	0.99943
PEAA-3	100	4.543	24.6	0.99985
	250	3.322	20.8	0.99988
	500	2.423	10.87	0.9988
	1000	1.321	5.78	0.99978
	2000	0.123	4.67	0.9996
	5000	0.0054	1.321	0.9993
	10000	0.00034	1.021	0.9982
PEAA-4	100	3.432	8.6	0.9965
	250	3.211	6.8	0.99943
	500	2.998	5.87	0.99985
	1000	2.576	5.78	0.99988
	2000	2.123	4.67	0.9988
	5000	1.342	4.321	0.99978
	10000	0.897	3.321	0.9996

Table (3.20): Rheological Data of KARAMA Crude Oil with PEAA Grafts at 36 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of KARAMA Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	60.85	79.5	0.9959
PEAA-1	100	11.323	24.6	0.99943
	250	11.112	20.8	0.99985
	500	10.786	19.87	0.99988
	1000	10.678	15.78	0.9988
	2000	8.341	13.67	0.99978
	5000	1.075	13.321	0.99991
	10000	0.00642	12.321	0.99967
PEAA-2	100	8.453	14.26	0.99987
	250	8.213	13.48	0.9999
	500	8.043	12.387	0.9999
	1000	7.8975	11.378	0.99943
	2000	6.564	11.267	0.99985
	5000	5.453	9.321	0.99988
	10000	5.198	8.321	0.9988
PEAA-3	100	14.543	44.16	0.99978
	250	13.322	40.28	0.99991
	500	10.423	30.187	0.99967
	1000	4.321	25.378	0.99987
	2000	1.123	14.167	0.9999
	5000	0.0094	8.321	0.9999
	10000	0.00084	6.321	0.99943
PEAA-4	100	13.432	18.16	0.99985
	250	13.211	15.18	0.99988
	500	12.998	13.17	0.9988
	1000	12.576	12.18	0.99978
	2000	12.123	11.87	0.99991
	5000	8.342	10.721	0.99967
	10000	5.897	10.421	0.99987

Table (3.21): Rheological Data of KARAMA Crude Oil with PEAA Grafts at 15 °C.

SAMPLE	Additive Conc. (ppm)	Rheological Data of KARAMA Crude Oil		
		Yield stress value Pa	Plastic viscosity mPa.S	Correlation Coefficient
Blank	0	76.9	92.34	0.9996
PEAA-1	100	19.323	35.16	0.99943
	250	18.112	30.48	0.99985
	500	16.786	26.77	0.99988
	1000	15.678	25.58	0.9988
	2000	11.341	23.97	0.99978
	5000	5.075	19.821	0.99991
	10000	0.03642	14.621	0.99967
PEAA-2	100	18.953	29.426	0.99987
	250	18.113	25.548	0.9999
	500	17.043	24.787	0.9999
	1000	16.8975	23.478	0.99943
	2000	9.564	21.667	0.99985
	5000	8.453	19.921	0.99988
	10000	5.198	12.421	0.9988
PEAA-3	100	24.543	65.316	0.99978
	250	21.322	51.987	0.99991
	500	19.423	41.387	0.99967
	1000	13.321	39.478	0.99987
	2000	2.123	35.1867	0.9999
	5000	0.0294	19.3621	0.9999
	10000	0.00684	12.5321	0.99943
PEAA-4	100	23.432	38.556	0.99985
	250	21.211	32.718	0.99988
	500	18.998	25.617	0.9988
	1000	14.576	24.318	0.99978
	2000	11.123	23.587	0.99991
	5000	10.342	20.921	0.99967
	10000	8.897	15.821	0.99987

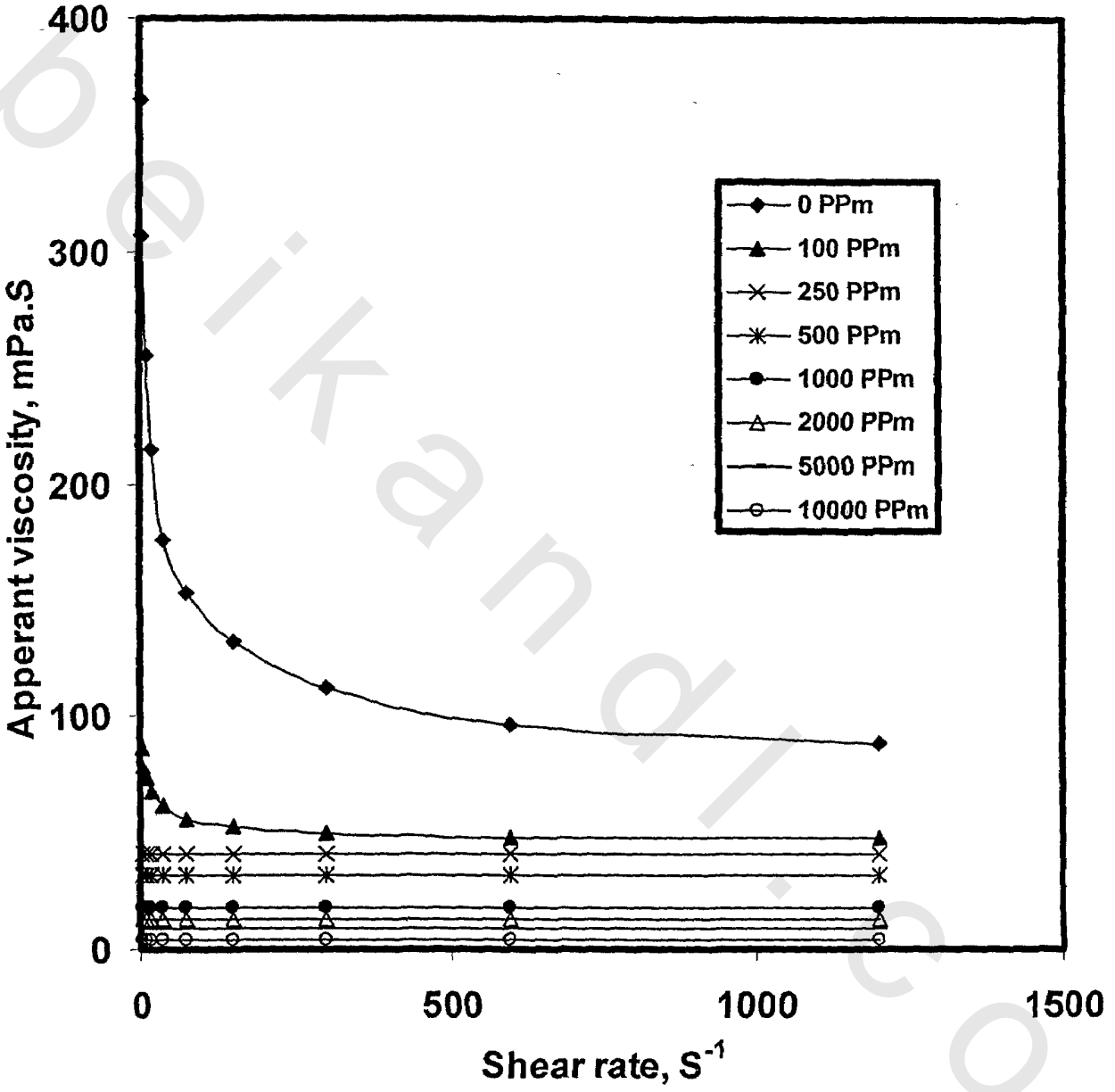


Figure (3.16): Effect of PEAA-4 on the Apparent Viscosity on BS Crude at Temperature 48 °C.

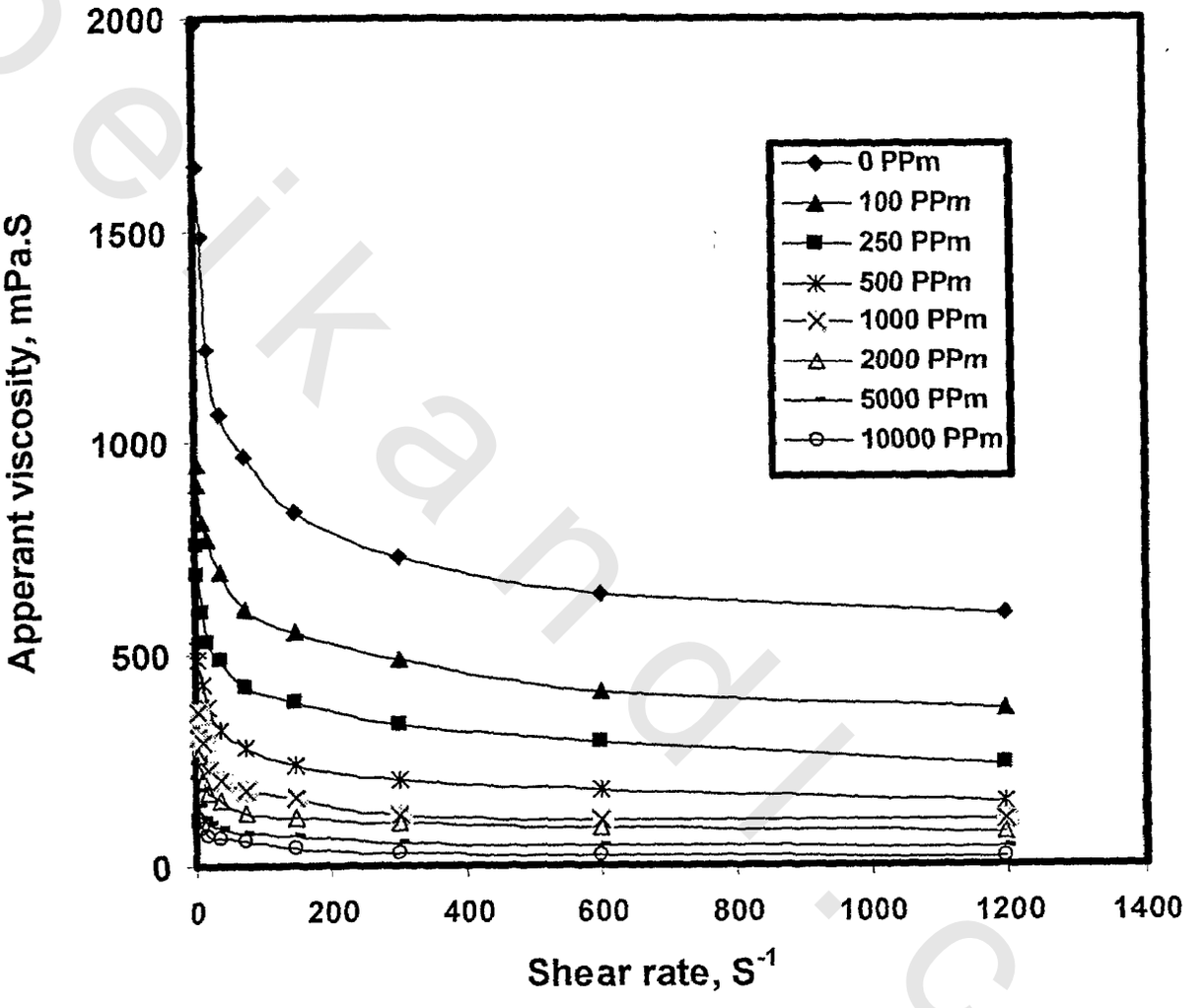


Figure (3.17): Effect of PEAA-4 on the Apparent Viscosity on BS Crude at Temperature 36 °C.

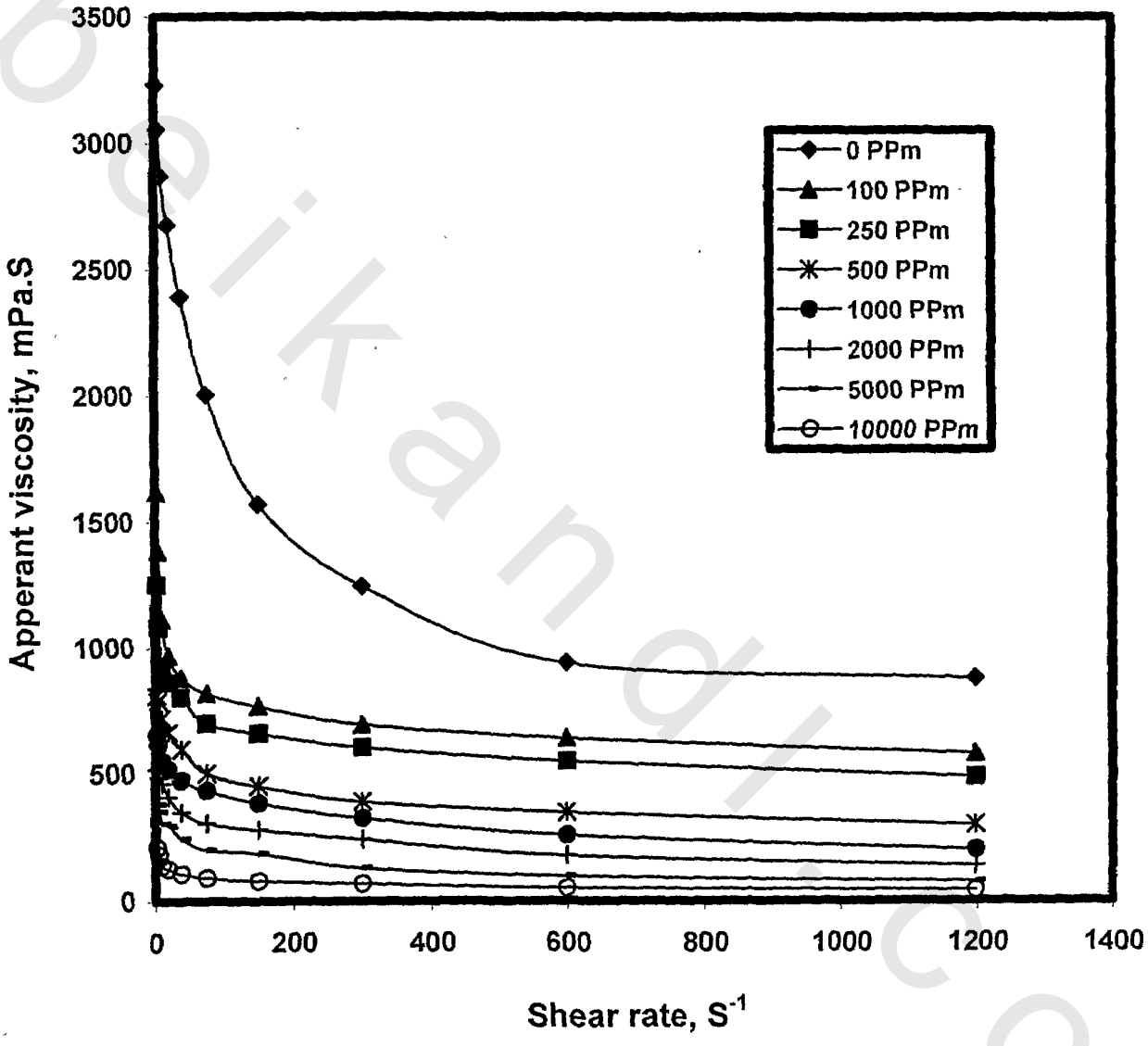


Figure (3.18): Effect of PEAA-4 on the Apparent Viscosity on BS Crude at Temperature 15 °C.

The pour point of a crude oil changes when an amount of additive precipitates together with the wax crystals modifying their morphology and inhibiting its aggregation; there is no shear during the experiment. Its rheological behavior, on the other hand, is a function of shear rate as well as of the concentration, shape and size of the solid particles dispersed in the system. As a result of such interaction the crystal aggregates formed are easily destroyed when the oil is submitted to shearing, producing particles whose size and shape are different and conducive to a different rheological behavior. However, as PEAA-2 presents a solubility parameter different from that corresponding to the crude oil, it does not precipitate the sufficient amount that would be necessary to significantly modify the wax crystals, and because of that PEAA-2 does not exhibit any efficiency as pour point depressant.

The idea that, in order to be efficient, an additive must present a cloud point close to the oil wax appearance Temperature (WAT) has been pointed out by various authors. **[163]** suggested three alternative mechanisms for wax inhibitors. The additive may come out of solution at a temperature slightly higher than the oil WAT and causes nucleation and small wax particles. The additive may come out of solution at the oil WAT and co-crystallizes with the wax, forming weak and deformed aggregates. Finally, if the additive comes out of solution at a temperature slightly lower than the oil WAT, it adsorbs on the wax crystals, inducing the

dispersion of the wax crystals. **[115]** described results reported by **[164]** in which it was shown that polymer additives crystallize before the paraffins and initiate the crystallization in the form of thin pyramidal lamellae or pseudo-spherical vesicles, on which paraffin crystals agglomerate in the shape of dihedra or hollow cones, making the wax cake weaker. Similar observations were reported by **[40]** in a work on the crystallization of wax from distillate fuels in the presence of pour depression additives. In this respect, polymeric solutions at 0.1 w/v% were used in this experiment. Diesel fuel was used as solvent for the prepared copolymeric additives, PEAA-1, PEAA-2, PEAA-3 and PEAA-4, and the cloud points were 45, 43 , 41 and 31 ^{o}C, respectively. Despite being very important for the additive performance, its precipitation from the solution together with the crude oil paraffin, does not seem to be the only factor that governs the phenomenon of organic deposition inhibition. The effect of concentration also represents an important point that, in our experiments, determines the different performance observed for PEAA-3 and PEAA-4. However, these differences may also have their origin in the polydispersity of both the polymer and the paraffin. From the preliminary results presented in this report, it may be inferred that for certain crude oils it seems possible to select an appropriate solvent representative of a crude oil solvent condition to assess the efficiency of paraffin deposition inhibitors. This procedure would be very useful to assess the performance of paraffin deposition

inhibitors and could also be used to orient the development copolymers formulations with the potential to prevent the formation of these deposits.

3.5.3. Effect of Temperatures on Rheology of Treated Crude Oils:

The viscosity of crude oil is perhaps an important physical property. For most crudes, at sufficiently high temperature, the viscosity at a given temperature is constant and the crude, although chemically very complex, is a simple Newtonian fluid. As the temperature is lowered, however, the flow properties of a crude oil can readily change from the simple Newtonian to very complex flow behavior due to the crystallization of waxes and the colloidal association of asphaltenes. The waxes basically consist of n-alkanes (nC_{17}-nC_{43}), which crystallize to form interlocking structures as plates, needles or mol-formed crystals. These crystals can entrap the oil into a gel-like structure that is capable of forming thick deposits in pipes and increasing pumping pressures to the point where flow ceases. Asphaltenes, on the other hand, a very large heterogeneous molecule with condensed aromatic nuclei can associate to form colloidal sized particles that strongly influence the viscosity of the oil medium and affect the crystallization of wax. The flow properties of oil containing crystallized wax are distinctly non-Newtonian. A yield shear stress can be many times higher than the normal pumping

pressure. Upon yielding, the flow properties show time dependency (the measured stress is not a constant at constant shear rate), indicating a degradation of structure with continued shear and finally show equilibrium or time-dependent flow properties, which still exhibit a yield shear stress and pseudoplastic behavior. In the present work, the rheological properties of three crude oils.

Figures (3.16-3.18) show the crude oil viscosity as a function of copolymer concentration at 48 and 24 °C, respectively. At 45 °C, the apparent viscosity is relatively low and none of the copolymer reduced the crude oil viscosity significantly, at the concentration range used. At 24 °C, it was observed that the copolymers reduced the crude oil viscosity and the results depended on type of the copolymer used. An important reduction in the apparent viscosity was observed for high concentration of copolymer, in particular for PEAA-1 and PEAA- 3. At a higher concentration, the viscosity reduction was higher for the crude oil containing PEAA- 3 and PEAA-1. PEAA-2 was the least efficient additive to reduce the crude oil viscosity although some reduction was observed for high concentrations. The best result was achieved for the crude oil containing 10,000 ppm of PEAA-3.

It is obvious that, the plastic viscosity and yield shear stress values decreased significantly with increasing concentration of each of all PEAA grafts. At 15 °C, the copolymers considerably reduced the crude oil apparent viscosity. In this temperature range, paraffin

crystals have already been formed in the liquid media and the rheological behavior of the oil is non-Newtonian. . It was observed that the PEAA-2 and PEAA-4 show non-Newtonian pseudoplastic relationships at temperatures from 36 °C to 15 °C. On the other hand, PEAA-3 and PEAA-1 additives show Newtonian relationship even at low temperature (15 °C) for all tested crude oils at concentration 10,000 ppm. Although PEAA-2 and PEAA-4 copolymers show non-Newtonian pseudoplastic behaviors at different concentrations and temperature, their yield shear stress and viscosity values were decreased as compared with untreated crude oils even at low temperatures. This indicates that PEAA copolymeric grafts have the ability to disperse wax crystals and improve the flow behaviors of the tested crude oils (as observed from the data listed in **Tables (3.13-3.21).**

3.6. EFFECT OF ADDITIVES ON FLOW OF CRUDE USING LABORATORY LOOP:

The crude oil produced in a number of basins deposit waxy paraffinic materials during production and transportation when subjected to a change in temperature and pressure. The extent of deposition can be manifested as damaged zones in the formation, in plugged tubing, flow lines and in sludge deposits at the bottom of the tank. These deposits in the wellbore can lead to restricted flow line pressure, decreased production and can cause mechanical problems **[165]**. This problem costs the petroleum

industry billions of dollars annually, in terms of cost of treatment, reduced production, wells shut-in, inefficient use of production capacity, choking of flow lines, premature abandonment and increased manpower **[166]**. Paraffins tend to precipitate when the temperature of the crude falls below the cloud point or the wax appearance Temperature (WAT). As the crude flows up the well bore, its pressure drops causing solution gas to liberate. This leads to a fall in temperature, increase in viscosity and a change in oil composition. All these factors aid in the precipitation of paraffin **[34, 167].** The deposition occurred as a result of lateral transport by diffusion, shear dispersion and Brownian motion. The temperature at the walls is less than the temperature at the center of the flow line. This leads to a temperature gradient and concentration gradient leading to molecular diffusion of the paraffin crystals toward the wall. In addition to diffusion, small particles of previously precipitated wax can be transported laterally by Brownian motion and shear dispersion.

The Reynolds number (**Re**) of the flow in the wells was calculated according the following equation

$$Re = (\rho D^n U^{2-n}) / k^{-} (8)^{n-1} \qquad (3.3)$$

Where **D, U** and **ρ** are internal diameter of pipe (m), velocity of crude (m/s) and density of crude (Kg m^3), respectively. While n is actual test speed of cup which determined from viscosity measurement and calculated from equation 2.2. The constant k^{-} is calculated from equation: $\mathbf{k^{-} = k\ (1+3n/4n)^n}$; where k is the

viscosity of crude oil. Re of BS, BS/20WR and KARAMA are calculated and found to be 2000, 1900 and 1800, respectively. Re of the tested crude oils and found to be <2100 which indicate the tested crudes have laminar flow characteristics. The flow rate in our experiments was manipulated to achieve a Reynolds number close to that of the crude in the transfer pipeline. Calculations indicated that, for the tubing used, with an internal diameter of 2.54 cm, this required a volumetric flow rate of 0.000221 m^3/s.

Four additives were suggested to mitigate the deposition of paraffin for the QPC obtained from this field. The pour point of the crude oils were found to be around 39-33 °C, while studies at the field indicated that the temperature of the flow lines could be as low as 7 °C. Therefore, the experiments were conducted by maintaining the temperature of the water bath at 7 °C, and thereby, the temperatures of the wall of the test section.

The first experiment (**Experiment 1**) was conducted without any additives in the crude and the heating temperature of reservoir was 45 °C. The deposition rate obtained would serve as a basis to compare the deposition rate obtained using the additives. **Experiment 2** was conducted by adding 10,000 ppm of additives to 0.07566 m^3 (20 gallon) of the crude in the reservoir tank. At the end of each experiment, the test section was disassembled and the volume of paraffin deposited was measured. **Experiment 3** was conducted to see the effect of the additive on the paraffin that is deposited already. Therefore, the experiment was conducted until

a sufficient amount of paraffin was deposited and then 10, 000 ppm was added.

In this work we describe a laboratory simulation of paraffin deposition using a specially designed flow-tube apparatus. This was used to determine the deposition from the QPC wax crude. Four paraffin inhibitors were obtained for these crude oils and used to mitigate the wax deposition in these experiments. The inhibitors were tested at concentration of 10,000 ppm as described from previous sections. The deposition rates were obtained for each of the inhibitors.

3.6.1 Calculations

The first task is to calculate the pressure drop indicated by the inclined manometer. The manometer is inclined at an angle of 35° to the horizontal and the manometric fluid is water. Therefore, the pressure drop would be

$$\Delta P = \Delta h g \rho \sin 35 \qquad (3.4)$$

where, Δh is the difference in the heights of the manometric fluid in the two columns in meters. **ΔP** would be in Pascal, "**g**" is the acceleration due to gravity and is equal to 9.81 m/s^2. "**ρ**"is the density of the manometric fluid which at this temperature was 1008 kg/m^3.

The diameter of the test section is 2.54 cm and its length is 1 m. The flow rate of the crude through the test section was maintained at 0.000221 m^3/s throughout the experiment.

The average velocity of the crude in the test section is then calculated using:

$$V = 4Q / \pi D^2 \qquad (3.5)$$

Where **V** is Average velocity, m/s and **Q** is Flow rate, m^3/s. Because the viscosity of the crude tended to increase slightly from experiment to experiment, it was calculated using the average velocity and the pressure drop.

The flow of the crude in the test section can be considered as laminar as the Reynolds number is less than 2100. The pressure drop can be calculated using the Hagen–Poiseuille equation, which is:

$$\Delta P = 32 \Delta L V \mu / D^2 \qquad (3.6)$$

Where, **ΔP** is Pressure drop, N/m^2 and g is Acceleration due to gravity (9.8 m/s^2).

Because the length of the test section and its initial diameter are known and the average velocity and the initial pressure drop calculated from measured data, the viscosity of the crude can be verified. The calculated viscosity can then be used to calculate the net diameter of the test section as the paraffin gets deposited on its walls.

The Hagen–Poiseuille equation is again used to calculate the net diameter of the test section during the deposition of paraffin. Eq. (3.6) is substituted to obtain

$$\Delta P = 128 \Delta L Q \mu / \pi D^4 \qquad (3.7)$$

Where μ is viscosity, PaS. Rearranging the terms to calculate the net diameter, we obtain

$$Dn = (128\Delta LQ\mu / \pi \Delta P)^{1/4} \quad (3.8)$$

The net diameter can be calculated as a function of time since the pressure drop can be noted at regular intervals. The net diameter can be used to calculate the volume V of paraffin deposition, m^3.

$$V = \pi/4(D^2i - D^2n) \Delta L \quad (3.9)$$

The following equation can be used to determine the thickness of the deposit on the tube (m).

$$t = (Di - Dn)/2 \quad (3.10)$$

where **Di** is initial diameter, m and **Dn** is net diameter, **m**. The calculated amount of paraffin at the end of the experiment can be compared to the amount of paraffin that is collected manually. The manometer readings obtained as a function of time were used to calculate the amount of paraffin deposition. At the end of **Experiment 1**, about 900, 800 and 700 μm^3 of deposit for BS, BS/20WR and KARAMA were collected on disassembling the test section and scraping out the deposit. The pressure drop measurements indicated that the deposition would be 820, 720 and 616.4 μm^3 for BS, BS/20WR and KARAMA, respectively. This discrepancy is possibly because the wax is not deposited evenly and also because a small amount of oil was entrained with the deposit when it was scraped and measured. Similar small discrepancies were noted for all the experiments conducted. All

the results show the amount of calculated wax deposited using eqs. (3.9) and (3.10).

In all three experiments presented, the temperature of the oil was held constant at 45 °C and the wall of the flow section was kept constant at 7 °C by cooling circulating thermostat using water. **Experiment 1** is the base case of the amount of deposition with no wax-inhibiting chemicals. For this case, 820, 720 and 616.4 ml of wax was deposited in 72 h for both BS, BS diluted with 20% of WR and KARAMA crude oils, respectively, by which time, the rate of deposition had leveled off. **Experiment 2**, was conducted at the same conditions but with increasing amounts of additives added to the oil to reduce the wax deposition to be 10,000 ppm.

In **Experiment 3**, we examined the effectiveness of using the solvent to break up wax after they have been deposited on the wall. Consequently, we allowed wax to deposit on the walls by flowing for 57 h without any wax-inhibiting solvent in the oil. Then, 10,000 ppm of additives was added to the oil and the experiment continued for another 15 h. We did not see any reduction in pressure during the final 15 h, indicating no reduction in the wax deposit. At the end of 72 h, the pressure drop indicated that the total wax have deposited, a statistically insignificant difference from the base case. Hence, this indicates that while PEAA-3 is somewhat effective in inhibiting wax deposition, it is not effective in removing wax that has already deposited.

The results of all the experiments are summarized in **Table (3. 22-3.23)**. Experiment 2 was conducted at the same conditions but at 10,000 ppm of PEAA and HDRA additives which added to the oil to reduce the wax deposition. It was noted that the quantity of the wax depositions was reduced with using 10,000 ppm of the additives. It was noted that a 73-35% reduction of wax deposition were determined from the base case. The data indicate that the efficiency of additives as wax deposition was found to be PEAA-3>PEAA-1>PEAA-4>PEAA-2. An economic analysis would have to be done to evaluate if these additives would be economically justified. The same experiment was conducted by replacement of the tested cold section with normal galvanized pipe to study the effect of additives on the flow of tested crude at static cooling from 45 to 25 °C. The experiment was hold at 25 °C for 24 h and carried out for the tested crude with and without additives. For both treated and untreated samples, the lab yield results are probably very conservative due to the use of dead oil and due to the effects of the pipe wall in the same diameter lab pipe loops. The applied pressure to restart the flow oil can be converted into a yield shear stress value by substituting the pipe loop dimensions into the above equation. The used test loop dimensions are: D and L are 2.54 and 100 cm, respectively. The applied pressure ΔP was determined from pressure difference between pressure at static cooling at 25 °C and restart pressure at this temperature.

Table (3.22): Summary of Experimental Results of QPC Crude Oils Using Lab Flow Loop with 10,000 ppm and without PEAA Additives.

Additives	Total wax deposited (ml)[1]			%Reduction[1]		
	BS	BS/ WR	KARA.	BS	BS/ WR	KARA.
Blank	820	720	616.4	0	0	0
PEAA-1	426	331	197	48	54	68
PEAA-2	508	432	339	38	40	45
PEAA-3	385	288	166	53	60	73
PEAA-4	533	454	370	35	37	40

[1] All these experiment were done with an oil temperature of 45 °C and a wall temperature of 7 °C for 72h.

Table (3.23): Experimental Yield Stress Results of QPC Crude Oils Using Lab Flow Loop with 10,000 ppm.

Additives	Calculated yield stress (psi)[1]		
	BS	BS/WR	KARA.
Blank	immeasurable	immeasurable	immeasurable
PEAA-1	0. 035	0.021	0.0089
PEAA-2	0. 042	0.027	0.00134
PEAA-3	0.031	0.018	0.0061
PEAA-4	0.044	0.029	0.0018

[1]All these experiment were done with an oil temperature of 45 °C and a wall temperature of 25 °C for 24h.

By substituting the loop dimensions and the applied pressure in equation (3.11) we get the yield shear stress: Ty= ΔP(0.00635) psi, then substituting the yield shear stress in equation (3.11) along with the pipeline dimensions we get the required pressure ΔP to yield the pipeline at 25 °C.

The results of yield shear stress (psi) was calculated and listed in **Tables (3.22** and **3.23)**. For the untreated crude oils, the yield stress values are immeasurable and beyond pump capacity. This behavior is mainly due to plugging of the loop at 25°C (below pour point temperature). While the reduction of yield shear stress for treated crude oil using additives have the order PEAA-3>PEAA-1>PEAA-4>PEAA-2. This order of reduction agrees with the previous result of pour point and cold finger deposition tests.