Use of Rosin-Based Nonionic Surfactants as Petroleum Crude Oil Sludge Dispersants

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ABSTRACT: The present work provides better knowledge for composition analyses of the sludge and evaluates the best effective and economical treatment of petroleum sludge. In this respect, nonionic polymeric surfactants based on rosin were prepared by esterification of rosin with different molecular weights of polyethylene glycol (PEG 400, 600, 1000, 2000) to produce rosin ester surfactants. The esterified rosin was reacted with maleic anhydride followed by reaction with diaminobutane or triethylene tetramine to produce rosin-imide. The products were etherified with PEG 600 and PEG 2000 to produce rosin-imide ERID-1, ERID-2, ERIT-1 and ERIT-2, which were characterized by FT-IR and ^{1}H-NMR analyses. The surfactants were tested as sludge dispersants from viscosity measurements of sludge crude oil mixtures at different times. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 183–192, 2011

Key words: rosin adducts; sludge dispersants; dispersant; petroleum crude oil sludge

INTRODUCTION

The petroleum sludge is composed primarily of asphaltenes that may form deposits during production, transportation, or handling of heavy crudes.[1–4] On the other hand, the waxy 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.[5] 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.

To effectively control asphaltene deposition, potential solutions for these problems include physical removal of deposits, solvent washes, and treatment with dispersant agents.[6] Usually, uses of nonionic amphiphiles, such as the ethoxylated nonylphenols, can be used for asphaltene stabilization process.[7,8] Blends of nonionic surfactants with ionic surfactants were used in sludge recovery.[9] The addition of ionic surfactants is important to increase cloud points of nonionic surfactants and, consequently increases the efficiency of these surfactants as sludge dispersants.[10] Petroleum sludge recovery and methods of sludge treatments are dependent on the chemical analysis and physical properties of sludge such as viscosity and melting temperatures.[11] Among the methods of sludge recovery, dispersants are used to disperse the sludge into fresh petroleum crude oil. The chemicals used for sludge recovery must give maximum separation for emulsified water (contaminated with sludge) as well as adequate dispersion of sludge into the fresh crude oil at low dose rate. In this respect, the detailed descriptive information in this work pertains to introduce advanced compositions, based on rosin, which may be useful in the synthesis of new dispersants. In the previous work[12] different types of nonionic surfactants based on rosin-imides (RI) maleic anhydride (MA) adducts that favored adsorption at interface more than micellization in bulk aqueous solution were prepared. In this respect, the present work aims to apply these surfactants as petroleum crude oil sludge dispersants.

EXPERIMENTAL

Materials

All materials were used without further purification. Rosin was heated at 150°C for 4 h, then heated at 200°C for 30 min in nitrogen atmosphere to isomerize rosin acids to levopimaric acid, and then it was

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TABLE I
Physicochemical Properties of the Tested Crude Oils

Test	Method	Value
API gravity at 60°F	ASTMD-1298	41.1
Specific gravity at 60/60°F	ASTM D-1298	0.820
Wax content (wt %)	UOP 46/64	16
Asphaltene content (wt %)	IP 143/84	3
Water content (vol %)	IP 74/70	0.23
Kinematic viscosity (cSt)	ASTM D-445	7
at 50–60°C		4.3
Pour point (°C)	ASTM-D97	33

separated by crystallization from the cold acetone solution of commercial rosin. Rosin acids with acid number 183 mg KOH/g and melting point 167°C was obtained from commercial rosin. The separation of the rosin acids from rosin was carried out to increase the yield and to remove terpens, which have the ability to react with MA. MA, triethylene tetramine (TETA), diaminobutane (DAB), β,β'-dichlorodiethyl ether, zinc dust, poly(ethylene glycol) having molecular weights 600 and 2000 designated as PEG 600 and PEG 2000, p-toluene sulfonic acid, and sodium hydroxide were supplied from Aldrich Chemicals Co. (USA) and used as received. N,N-dimethylformamide (DMF) was analytical grade and purchased from Aldrich.

The sludge used in the present investigation was separated from storage tanks of Qarun Petroleum Co. (Egypt). The asphaltene percent, clay and sand contents, water, inorganic salts and wax contents were found to be 26, 10, 4.5, and 53 wt %, respectively. Base crude oil from Qarun Petroleum Co. (Egypt) was used as diluents to dissolve the petroleum sludge. Table I lists the specifications of these crude oils.

Monomer synthesis

Preparation of rosin ester-maleic anhydride adducts (RMPEG)

Rosin (1 mol) was placed in a glass reactor and heated to 220°C on a heating bath. PEG 600 (1.1 mol) or PEG 2000 (1.1 mol) was mixed with this molten mass using a glass stirrer. The temperature of the mixture was maintained at 240°C till the completion of reaction. Zinc dust (0.5%) was added as catalyst. Acid number of the mixture at every 1-h interval indicated fate of reaction, and the insignificant difference between the two successive acid numbers confirmed its completion. Further, the reaction temperature was allowed to cool at 140°C. MA (1 mol) was added to this melt and the reaction was continued for 1 h. The molten mass was poured on steel plates, allowed to solidify, powdered, washed thoroughly with water, and air dried.

Rosin PEG ester-maleic anhydride adducts with PEG600 or PEG 2000 can be designated as RE-MA1 or RE-MA2, respectively.

Preparation of rosin-imides (RI)[12]

RI may be prepared as follows: TETA or DAB (15 mmol) was diluted in 6 mL of DMF in a flask fitted with a water condenser with a drying tube, a thermometer, and an N_2 purge tube. RE-MA1 or REMA2 (10 mmol), was dissolved in 10 mL of DMF and the solution added to the diamine solution dropwise at 80°C with stirring. During addition, the temperature of the reaction mixture was raised to 135°C and kept there for 2 h. Water formed during imidization was removed by distillation with DMF, while fresh dry DMF was added to the reaction mixture continuously. The RI were precipitated with diethylether to remove unreacted RE-MA1 or RE-MA2 and TETA or DAB. It was finally dried at 40°C under vacuum. The monomers produced with TETA and DAB were designated as RIT-1 or RIT-2 and RID-1 or RID-2, respectively. RID-1, RIT-1, RID-2, and RIT-2 monomers were light brown powders; yields were 85, 90, 88, and 95%; melting points were 90, 65, 110, and 78°C and nitrogen contents were calc. 2.64; found 2.55, calc. 5.01; found 5.22, calc. 1.92; found 1.88, and calc. 3.70; found 3.75, respectively.

Etherification of RIAAT and RIAAD[12]

In a 250-mL three-necked flask fitted with condenser, mechanical stirrer, and thermometer the RIT-1 or RIT-2 and RID-1 or RID-2 monomers (0.1 mol), β,β'-dichlorodiethyl ether (0.2 mol), PEG (0.2 mol), NaOH (0.4 mol), and DMF (100 mL) were added together with stirring. The reactants were agitated and slowly heated to a temperature of 170°C. The reaction mixture was maintained at this temperature for 5 h. The progress of the reaction was evaluated by determining the NaCl content that increases gradually to reach a constant value at the end of the reaction. The product was treated with an equal volume of saturated NaCl solution and neutralized with dilute HCl. Then, the reaction mixture was filtered to separate NaCl precipitate and the product was dried from DMF under vacuum.

CHARACTERIZATION OF PETROLEUM SLUDGE

About 50 g of sludge was extracted with 300 mL of toluene using Soxhlet extractor. The extraction continued for 12 h, or until colored extracts ceased. Water collected in the side-arm receiver was drained in a preweighed beaker and its weight was obtained. The flask containing the extracts was connected to a

rotary evaporator extractor and toluene was distilled under mild vacuum. The weight of residual toluene soluble organics (TSO) (bituminous-like material) was determined. Weight of toluene insoluble matter (TIM) in the porcelain crucible was determined. The paper thimble containing TIM was placed in an ordinary Soxhlet system and was extracted with 150 mL of tetrahydrofuran (THF) for 3 h (or until colorless extracts are observed). THF was evaporated and the weight of heavy asphaltenic fraction (HAs) was determined. TIM was reweighed to get the final inorganic fraction (INORG). TSO (3 g) was placed in a 250-mL conical flask. TSO was wetted with 1 mL of benzene or toluene and100 mL of the alkane solvent (n-pentane or n-heptane) was added. The mixture was agitated at room temperature for 2 h using a supersonic shaker. The precipitated organics (insoluble) were filtered using a Buchner funnel and precipitate was washed with 3×20 mL portions of the same solvent. Insoluble fraction was dried for 2 h at 105°C, cooled in a desecrator, and weighed. The soluble organics fraction was determined by evaporating the solvent, drying at 105°C for 2 h, cooling, and weighing. Percent loss was calculated.

Accurately weighed 0.5 g samples of sludge containing TSO, TIM, insoluble asphaltene in n-pentane fraction (n-C_5As), insoluble asphaltene in n-heptane fraction (n-C_7 As), n-pentane, and n-heptane (n-C_5 and n-C_7) soluble materials were ashed at 900°C for 3 h using a muffle furnace. Ashing and weighing continued until constant weight was obtained.

Measurements

C, H, N analysis was carried out on sludge, TSO, n-C_5 As, n-C_7As, and H As using CARLO ERBA INSTRUMENT MOD. 1106.

Infrared spectra of the prepared compounds were recorded in polymer KBr pellets using Mattson-Infinity series FTIR Bench Top 961.

^{1}HNMR spectra of prepared resins were recorded on a 270-MHz spectrometer W-P-270 and Y Brulker using $CDCl_3$ solvent. Molecular weights of epoxy resins were determined by using a Muffidetector GPC Waters 600-E equipped with Styragel column.

Trace metal analysis was carried out on parent crude oils, sludge and INORG II, using atomic absorption spectrophotometer model: VARIAN A-A 1475. Sulfur analysis was carried on sludge, TSO, n-CsAs, n-C7 As by the pump method.

EVALUATION OF THE PREPARED SURFACTANTS AS SLUDGE DISPERSANTS

The sludge was mixed with Qarun petroleum crude oil with ratio 50%. The sludge and crude oil mixture were heated up to 65°C, and the mixture was maintained at this temperature until the sludge solubilizes in the crude oil. The blends (blank) were poured in the reagent bottle and heated in water bath at 65°C until the water was separated from sludge/crude oil blends.

The purified surfactants were dissolved in toluene at concentration of 25% (wt. of surfactants/volume of toluene). Toluene was used as carrier for surfactants in the petroleum sludge. The surfactant solutions were used to treat the petroleum sludge with fresh petroleum crude. The prepared surfactant solution was added to the blank with ratios of 2.5, 5, 10 wt %. The flow time of the blend was measured using Saybolt viscometer for 3-days per week to evaluate the dispersion capability of the prepared surfactants as sludge dispersant.

RESULTS AND DISCUSSION

Gum rosin, which contains $\sim 90\%$ of abietic acid, is treated in a number of ways according to its applications. Gum rosin is made to react with MA to form the Diels–Alder adduct. The Diels–Alder adduct, MPA, is also known as maleopimaric acid. The molecule of MPA contains one carboxyl group and one anhydride group. The two reactive functionalities are capable of undergoing various chemical reactions with appropriate reagents.[13] Accordingly, the present work aims to prepare nonionic surfactants based on rosin gum to apply as sludge dispersants. In this respect, nonionic surfactants based on rosin ester of rosin acids with PEG having different molecular weights 400, 600, 1000, and 2000 g/mol were prepared. Modification of rosin ester with PEG 600 and 2000 through 1,4 Diels–Alder addition with MA followed by synthesis of rosin-imide adduct using TETA and 1,4-diaminobutane was conducted according to the experimental section. Finally, application of the prepared surfactants as sludge dispersants is discussed in the forthcoming sections.

Preparation of nonionic surfactants

The present work deals with synthesis of nonionic surfactants by reacting the carboxylic acid of rosin acid with PEG. The esterification of rosin acids with PEG is used to increase the hydrophilicity of the rosin acids. Addition of zinc granules significantly increased the esterification reaction rate between rosin and PEG. In this respect, four different molecular weights of polyethylene glycol (PEG), namely, PEG 400, 600, 1000, and 2000 g/mol, were reacted with rosin to produce the surfactants R-EO9, R-EO13, R-EO23, and R-EO45, respectively. The numbers (n) 9, 13, 23, and 45 are referred to number of ethylene oxide groups in PEG. The structures of the produced surfactants were confirmed by using IR spectroscopy. It was observed that the spectra of all R-EO
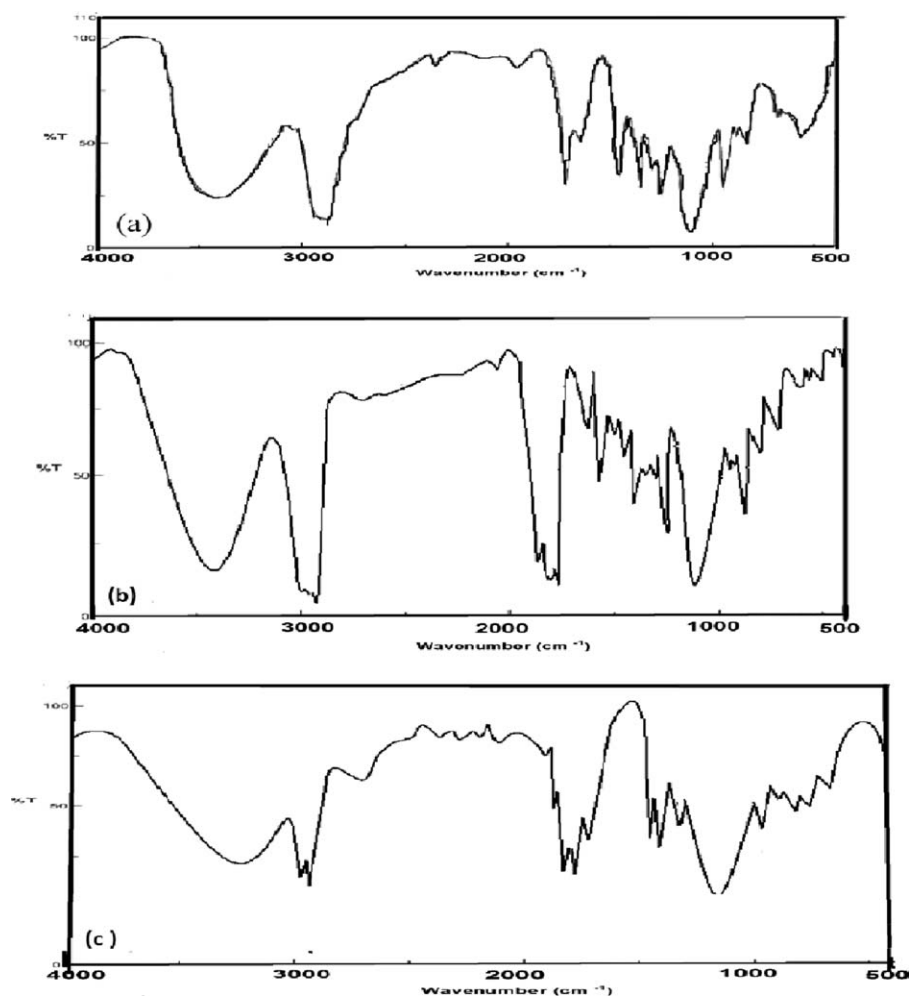
Figure 1 FTIR spectra of (a) R-EO9, (b) RE-MA, and (c) ERID-1 surfactants.

derivatives are nearly identical. Accordingly, a representative infrared spectral patterns of R-EO9 was represented in Figure 1(a) The stretching bands at 3450, 1745, and 1100 cm^{-1} for OH, carbonyl (C=O) of ester and C—O ester were observed in all spectra and indicated the formation of rosin-PEG esters. These esters were soft at room temperature and difficult to handle. However, addition of MA improved the physical characteristics of the products. In this respect, this work aims to select R-EO13 and R-EO45 esters to react with MA to produce rosin ester-MA Diels–Alder adducts. The sequence of reaction taking levopimaric as model component is given in Scheme 1. The concentration of PEG 600 in the reaction mixture proportionally converted resin acids into esters and exhibited reciprocal relationship with the acid number. As the concentration of PEG 600 in the reactant mixture increases, more of the resin acids are converted into PEG ester of higher molecular weights. Polydispersity value of RE-MA nearer to one indicated uniformity of the reaction product. The condensation of DAB and
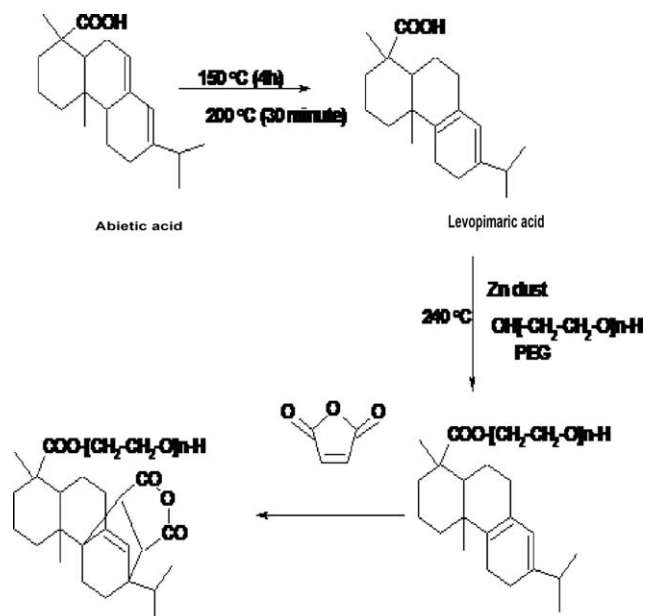
Scheme 1 Scheme of synthesis of RE-MA adducts.
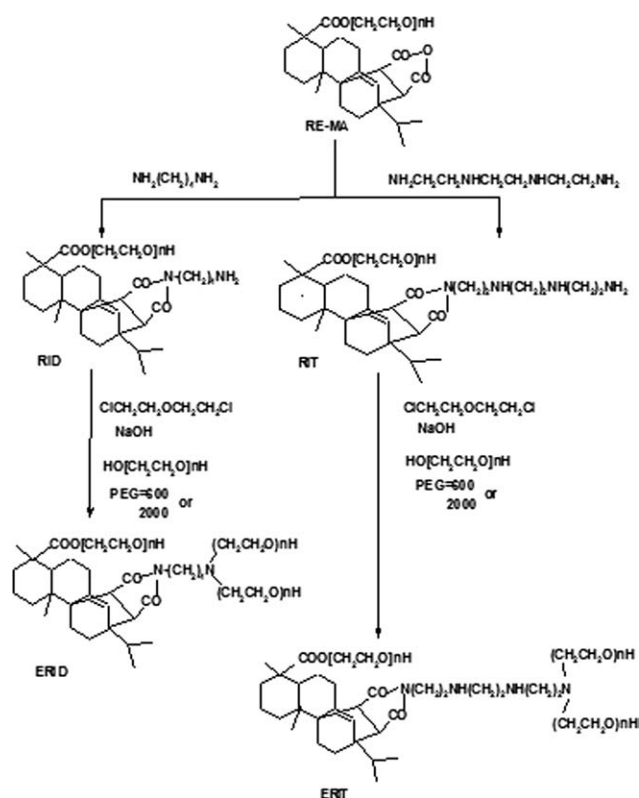
Scheme 2 Scheme of synthesis of ERID and ERIT surfactants.

TETA with RE-MA can be schematically represented in Scheme 2. The products were found to be soluble only in highly polar solvents such as dimethyl formamide, dimethyl sulfoxide, m-cresol, and so forth. The FT-IR spectra of RE-MA and ERID-1 were represented in Figure 1(b,c), respectively. FTIR spectrum of RE-MA was represented in Figure 1(b), indicated the appearance of two bands at 1790 and 1870 cm^{-1} that attributed to the anhydride C=O and a broad band at 3300–3400 cm^{-1} due to the stretching vibration of —OH. The characteristic IR bands of the RI [Fig. 1(c)] are observed near 1725, 1785, and 725 cm^{-1} for the cyclic imide group. The peak for the olefinic double bond appears at 1625 cm^{-1}. The broad band at 3300–3400 cm^{-1} is due to the stretching vibration of O—H system present in the ERID. However, in addition to

these two peaks, the IR spectra of all the derivatives show C=O stretching at 1740 cm^{-1} suggesting the formation of ester. It was observed that the spectra of all derivatives are nearly identical. IR analysis was used to confirm the etherification of amine at two ends. In this respect, it was observed in all spectra the disappearance of one of the two sharp bands at 3350 cm^{-1} for NH and appearance of new band at 1540 cm^{-1} for C—N stretching vibration of the tertiary amine.

Nonionic rosin-imide polymeric surfactants were prepared from the etherification of RID and RIT monomers by using β,β′-dichlorodiethyl ether and PEG 600 and PEG 2000 as reported in the experimental section. The etherified products of RID and RIT with PEG 600 and PEG 2000 can be designated as ERID-1, ERID-2, ERIT-1, and ERIT-2, respectively. The numbers 1 and 2 can be attributed to PEG 600 and PEG 2000, respectively. Etherification of rosin-imide with polyethylene having molecular weights 600 and 2000 g/mol in presence of β,β′-dichlorodiethyl ether to produce nonionic polymeric surfactants was represented in Scheme 2. The strategy of synthesis is based on preparation of polymeric surfactants having different hydrophile–lipophile balance (HLB) to study effect of surfactant structure on its properties. The physicochemical properties of the rosin derivatives were illustrated in Table II. ^{1}H-NMR of RE-MA in Figure 2(a) he protons of oxyethylene units at δ = 3.6 ppm, —OH proton of PEG at 4.3 ppm ^{1}H-NMR spectrum of ERID-1 were selected and represented in Figure 2(b). The protons of oxyethylene units at δ = 3.6 ppm, —OH proton of PEG and N-(CH$_2$CH$_2$)n-N at 4.3 ppm are observed in the spectra of all surfactants. Signal of methylene (CH$_2$)$_n$, appearing as an intense broad band at δ = 1.35 ppm, was used to assign the incorporation of aliphatic diamines in the structure of the prepared surfactants.

EVALUATION OF THE PREPARED SURFACTANTS AS SLUDGE DISPERSANTS

Among the methods of sludge recovery, dispersants are used to disperse the sludge into fresh petroleum crude oil. In the last couple of decades, considerable effort has been devoted to developing chemical

TABLE II
Physicochemical Properties of the Prepared ERI Surfactants

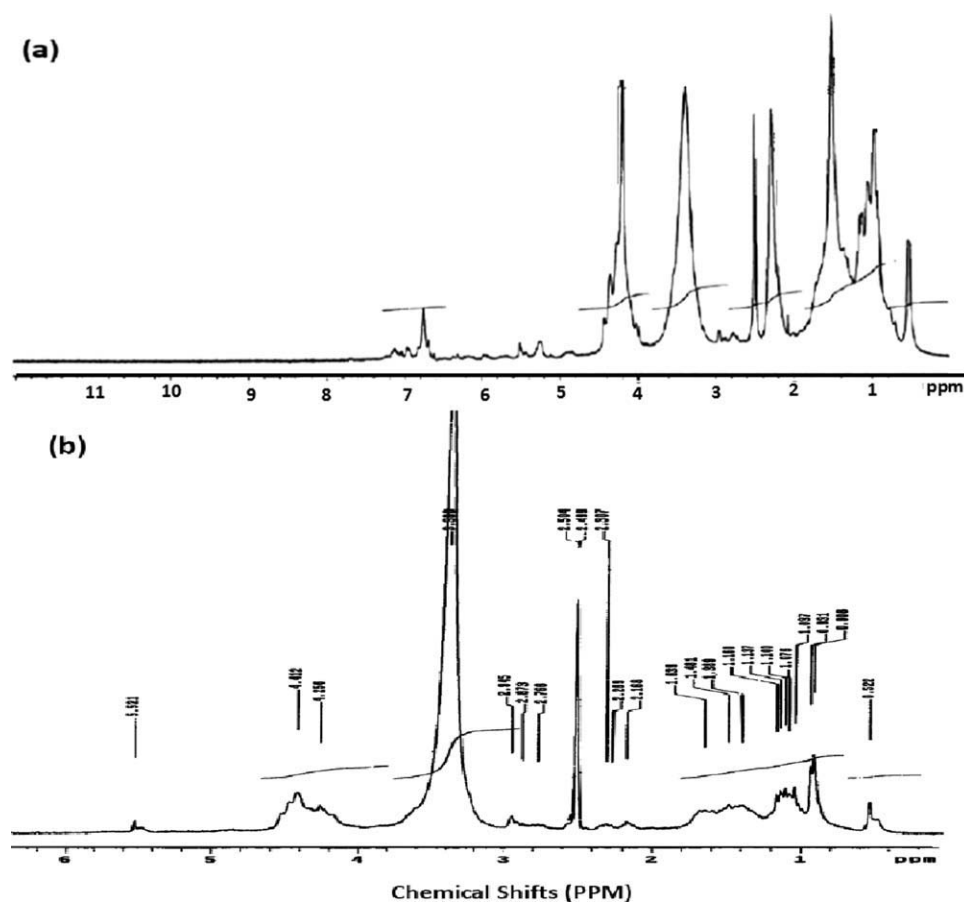|	Nitrogen content (%)		Molecular weight GPC analysis (g/mol)		
Designation	Calc.	Found	Number average (Mn)	Weight average (MW)	Yields (wt %)
ERID-1	1.22	1.25	2310	2772	93
ERIT-1	2.38	2.44	2410	2892	90
ERID-2	0.80	0.83	3530	4236	85
ERIT-2	1.58	1.62	3610	4512	80

Figure 2 ^{1}HNMR spectra of (a) RE-MA and (b) ERID-1 surfactants.

methods of inhibiting paraffin deposition. The chemical inhibitors can be broadly classified into four categories. Solvents contain high aromatic compounds used for dissolving paraffin. Second, wax crystal modifiers inhibited or alter wax crystal growth. Third, paraffin dispersants inhibited the particles from uniting and depositing. Fourth, asphaltene dispersants and stabilizers are widely used in hard sludges or asphaltenic sludge. The use of chemical inhibitors to reduce the paraffin problem has become popular in the industry. Although a number of chemicals are known that possess paraffin inhibition properties, it was observed that no single chemical was equally effective in all wells. There were instances when a particular chemical performed well in one well but failed in another well in the same basin. Therefore, it is required to find the best inhibitor for each well individually.[14]

Chemical analysis of the sludge

Petroleum sludge recovery and methods of sludge treatments are dependent on the chemical analysis and physical properties of sludge such as viscosity and melting temperatures.[15] In this respect, sludge materials were analyzed as reported in the experimental section. Composition of sludges from storage tanks of various crude oils have been reported.[16] Toluene is used to dissolve the organic matter and azeotrope water in one operation. Ultimate analysis (C, H, N, S, and O) and percent ash determination were conducted on the TSO. This matter was further fractionated by n-alkane solvents; n-pentane and n-heptane; to soluble and insoluble subfractions. Ultimate analysis and ash content were conducted on the subfractions. The TIM was further fractionated with THF to obtain a HAs and an inorganic residue (INORG.). The concentration of some of trace metals in total sludge and in inorganic residue was also determined by atomic absorption spectroscopy. At the end of extraction all TSO were accumulated in the round bottom flask, the toluene insolubles stayed in the thimble and azeotroped water (AzW) in the side-arm connection. TSO was recovered by evaporating the solvent under a mild vacuum in rotary evaporator equipment. Table III gives the results of several analyses conducted on the sludge studied in this work, namely Qarun sludge that was extracted from Qarun storage tanks. A homogenized sample of the sludge was obtained by mixing 50 g of each sludge (which have been taken from different storage tanks) put in a beaker, followed by heating to

TABLE III
Analysis of the Qarun Sludge

Sample no.	Fraction			% of asphaltenes on TSO basis	
	TSO	TIM	AzW	Pentane AS.	Heptane AS.
1	88.9	8.4	1.7	27.7	29.9
2	91.7	6.2	2.1	24.4	21.6
3	88.4	9.9	1.5	22.7	21.9
4	90.0	9.9	1.8	27.7	23.5
Average	89.3	8.6	1.8	25.6	24.2

about 75°C with a vigorous manual stirring. The analysis of the homogenized sample is given in Table IV. The elemental analysis of TSO and its subfractions and their ash contents[17] in addition to that of the parent sludge are given in Table V. The concentration of some heavy metals in sludge was obtained by atomic absorption measurements. Table VI gives the concentrations in total sludge and in the inorganics after stripping the organics with toluene and THF (refer to INORG-II). Throwing some light on the correlation between some of the sludge properties with those of the parent crude oil helps in understanding the mechanism of sludge formation. Physicochemical properties of the crude oils were measured as described in the experimental section and listed in Table I. The fluctuation in the results in Table III on % TSO and % TIM are expected because of the difficulties in homogenizing the highly viscous, semisolid physical state of the sludge that forms pockets of heavy liquid and air bubbles and sometimes small pools of water on homogenizing by hand. Added to this, accumulation of sludge over a period of many years in a desert atmosphere under extreme temperature variations, rain, dust and sand storms, have strong impacts on the physical and chemical properties of sludge components.[18] Results on the separation of n-C5 and n-C7 insolubles from TSO on samples from Qarun sludge showed a higher ratio of n-C5 insolubles. On the other hand,

the order is reversed in the n-C7 insolubles. The results in Table IV on the extraction of organics by toluene (TSO) or by tetrahydrofuran (THF-SO) from a homogenized sludge sample, confirm the stepwise extraction data given in Table III where an adjustment was necessary to account for light end loss during toluene mild vacuum stripping in the stepwise operation. The other results on the inorganic remainder, amount of water distilled and light ends distilled with water fit reasonably well with the corresponding data given in Table III. Further calculation on the H/C, N/C, and SIC ratios from the ultimate analysis data given in Table V, were represented in Table VII below. These ratios were calculated for the total sludge, TSO, and n-C7 insolubles in the Qarun sludge under investigation. The results on trace metal analysis in parent crude oils, in a homogenized sludge sample and in inorganic isolated from the homogenized sample by THF extraction (INORG. II) are given in Table VI. On the basis of the magnitude of total inorganics, after the THF extraction being 4.45% (Table IV), it can estimate the percentage distribution of each trace metal among the inorganic residue and the organic extract from the homogenized sample. It is well established that exposure of crude oil constituents to ambient conditions during prolonged storage increases the oxygen function in the oil through various methods of oxygen incorporation. Consequently, this causes an increase in polarity of some constituents and the conversion of aromatics to resins and resins to asphaltenes. The presence of small amounts of original connate water in stored crude oil, even after dewatering, functions as a nucleus for sludge

TABLE IV
Analysis of Homogenized Qarun Sludge Sample

Component	Total percent
Toluene soluble organics (TSO)	84.14
Asphaltene content	26
Wax content	53.5
Heavy asphaltenic matter (THF extract from TIM)	1.30
Organic totally extracted by THF (THF.SO)	87.10
Inorganic remained after extraction with toluene	4.54
Inorganic remained after extraction with THF	4.45
Water separated by distillation	10
Light hydrocarbons distilled with water	4.8
Sludge pour point (°C)	65

TABLE V
Elemental Analysis and Ash Content of Qarun Sludge and Their Subfractions

Component or fraction	Percent element (%)					Percent of ash
	C	H	N	S	O	
Total sludge	77.06	12.09	0.60	0.34	9.44	4.85
TSO	81.72	13.34	0.71	1.60	2.66	0.01
n-heptane insoluble	82.05	13.48	0.66	0.59	3.23	0.01
n-heptane soluble	–	–	–	0.53	–	–
TIM	14.82	2.21	0.16	–	–	70.74

TABLE VI
Concentration of Some Heavy Metals in Sludge Material Measured by Atomic Absorption

Metal	Concentration (ppm)		
	Total sludge	Inorganic II	Qarun sludge
Cd	0.1	0.08	0.08
V	8.5	34.7	1.62
Ni	11.4	100	0.13
Pb	19.3	460	2.77
Mn	42.6	620	0.01
Zn	257	8170	0.04
Fe	1700	17,300	2.94

TABLE VII
Elements Ratios in Sludge and Some Fractions

Component	H/C	N/C ($\times 10^{-3}$)	S/C ($\times 10^{-3}$)
Total sludge	2.01	6.7	1.7
TSO	1.96	7.5	7.3
n-C7 insolubles	1.97	6.9	2.6

formation resulting in deposits accumulating at the bottom of storage tanks. The mechanisms of deposits formation is suggested here. Dissolved inorganic ions in suspended water droplets attract oppositely charged centers in petroleum components such as those in asphaltenes, resins, and oxidized constituents (Scheme 3). This mechanism suggests that organic matter in sludge (e.g., TSO) contains high percentage of asphaltic and resinous materials. It is correctly the case as it is evident from the results in Table V. Normal heptane insoluble rose from 0.30 to 0.73% in Qarun and in their sludges, respectively. Water content of sludge is evident from the results in Tables V and VI. Sludge deposits also contain inorganic fines, either indigenous driven out with crude oil as a result of high pressure, or as a result of precipitation from their supersaturated solution in connate water after cooling to ambient temperature. Dust storms and rain may contribute to increasing fines and water contents on long storage times. It is also expected that some high molecular weight alkanes, cycloalkanes, and aromatic hydrocarbons will settle down with the polar centers presented in Scheme 3. This depends on one of the rules of solubility "Like Dissolves Like," where the alkyl portion in asphaltene or resins is usually dissolved in (surrounded by) high molecular weight hydrocarbons, some of which will settle down as a sludge component. The data of the sludge analyses indicated that, the toluene affected the removal of over 90% wt, of sludge constituents as a viscous, bituminous-like organic matter that leaves only trace amount of ash after combustion. This toluene soluble matter (TSO) comprises about 25% asphaltene compounds, precipitated by n-pentane or n-heptane. The remainder 75% of TSO weight is of heavy maltenic nature. The chemical composition of TSO in Qarun sludge seems to be relatively "rich in hydrogen content" and heteroatom N and S contents increased markedly compared to the parent crude oils. Nitrogen and sulfur seem to be randomly distributed in Qarun sludge and its subfractions TSO and n-C, insolubles. TSO contain most of nickel (Ni), one-half of vanadium (V), one-half of iron (Fe), and one-third of manga-

nese (Mn), which are present in parent sludge material. On the other hand, the inorganics in the sludge contain noticeable amounts of lead (Pb) and zinc (Zn). Dissolved inorganic in the associated water, whether original connate water from the reservoir or surface water, in the stored crude oil play a major role as a nucleus for the accumulation of heavy and polar constituents that in time settles down in the form of a sludge. It is thus concluded that efficient dewatering of crude oils before storage may minimize their sludge formation tendency.

Flow time measurements of the treated sludge

The chemicals used for sludge recovery must give maximum separation for emulsified water (contaminated with sludge) as well as adequate dispersion of sludge into the fresh crude oil at low dose rate. In this respect, the solubility of the prepared surfactants in toluene and gas fuel oil was determined and it was found that all prepared surfactants were solubilized in toluene and gas fuel. The solubility of the prepared surfactants indicates that all surfactants can be used as sludge dispersants into fresh crude
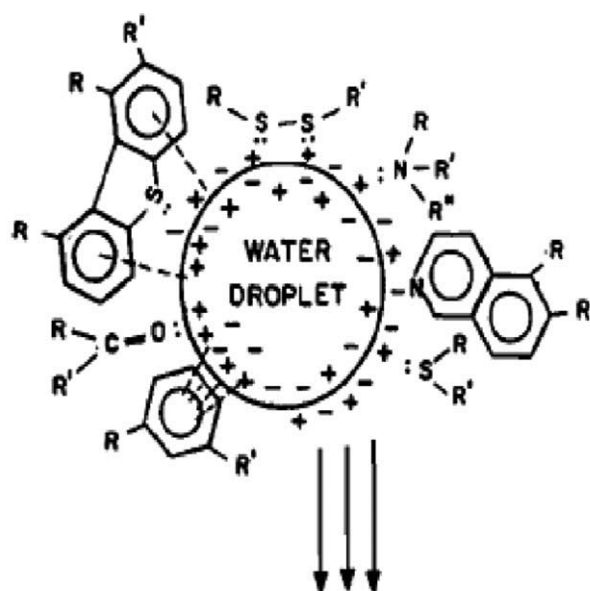
Scheme 3 Polar species attracted by changes on water droplet and pulled down by gravity.

TABLE VIII
Dispersion Stability Data of Sludge/Crude Oil Mixture in the Presence of 10% of the Prepared Surfactants

Designation	Flow time (s) after 1 day	Flow time (s) after 2 days	Flow time (s) after 3 days
R-EO9	70	73	75
R-EO13	65	68	70
R-EO23	74	72	74
R-EO45	78	80	85
ERIT-1	65	67	70
ERIT-2	77	81	86
ERID-1	60	62	65
ERID-2	80	87	90

TABLE X
Dispersion Stability Data of Sludge/Crude Oil Mixture in Presence of 2.5% of the Prepared Surfactants

Designation	Flow time (s) after 1 day	Flow time (s) after 2 days	Flow time (s) after 3 days
R-EO9	96	100	103
R-EO13	100	107	115
R-EO23	105	110	123
R-EO45	106	116	130
ERIT-1	90	95	97
ERIT-2	101	115	125
ERID-1	85	88	89
ERID-2	105	120	128

oil. The chemical analysis of sludge, as determined in experimental section, classified the evaluated sludge as waxy. For this reason, Wadi Elrayan (Qarun Petroleum Company, Egypt) petroleum crude oil can be used to study the ability to use the prepared surfactants as sludge dispersants. In this respect, viscosity of treated sludge at 25°C for both fresh and mixed petroleum crude with different ratios of sludge at surfactants doses 2.5–10 wt % were determined and listed in Tables VIII–X. The viscosities of sludge and crude oil blends (50% of sludge and 50% of Qarun mix crude oil) in the presence of dispersants were evaluated during 3 days to test the dispersion stability of dispersants as petroleum sludge recovery. Sludge dispersants doses were related to sludge volume for all dispersants. It was observed that the sludge is not soluble in the crude oil without surfactant additives at temperature of treatments (60°C), while the solubility of the sludge into crude oil was enhanced by addition of the prepared surfactants. Accordingly, the viscosity of the blank was not immeasurable at ambient temperature. It has been reported that the dissolved dispersants in organic phase afford more stable dispersions. It can be seen that the dispersion stability data Tables VIII–X confirm the above argument. This is attributed to the fact that the organic phase is a good solvent for the backbone as well as for the

TABLE IX
Dispersion Stability Data of Sludge/Crude Oil Mixture in Presence of 5% of the Prepared Surfactants

Designation	Flow time (s) after 1 day	Flow time (s) after 2 days	Flow time (s) after 3 days
R-EO9	80	83	84
R-EO13	84	88	90
R-EO23	90	92	95
R-EO45	95	100	100
ERIT-1	72	74	75
ERIT-2	85	90	92
ERID-1	68	69	70
ERID-2	90	93	95

PEG side chains, and rosin have an expanded conformation, which acts perfectly for stabilizing asphaltene droplets. The data listed in Tables VIII–X show that the surfactants having low HLB and low molecular weights based on PEG or EO are more effective as demulsifiers than other surfactants. This behavior can be explained on the basis of the relation between HLB of surfactant and its solubility in the oil phase (dispersed phase). When the surfactant is initially introduced to the oil-in-water emulsion, it will be more thermodynamically stable at the interface of the water droplets. Accordingly, the surfactants possess low HLB and migrate faster to the interface than those having higher HLB. As a result of such enhanced migration toward the interface, the surfactants form a continuous hydrophilic pathway[19] existing between the dispersed water droplets. This leads to a rupture of the asphaltene interfacial film surrounding the water droplets. The viscosity data indicate that the best ratio between fresh crude oil and sludge is 50 : 50 wt %. R-EO9, RF-SA-EO45, RF-EO13, ERID-1, and ERID-1 show low viscosity values than other surfactants when added to crude oil sludge blends. This behavior indicates that ERID-1 possesses good dispersion efficiency. To improve the understanding of the surfactant activity as asphaltene stabilizers, it is needed to gain insight into the interactions between asphaltene, surfactant, and solvent. It has been reported that[20] the activity of surfactant as asphaltene stabilizer is related to the asphaltene–surfactant interactions and to the capability of the surfactant to form a stabilization layer around asphaltene particle. Recently, it has also been reported[21] that the effectiveness of a series of alkyl benzene surfactants as asphaltene stabilizers is related to the extension of the adsorption of these surfactants on the asphaltene surface, dispersion medium, and type of crude oil. In the present study, the data of the sludge dispersants can be correlated with thermodynamic parameters of micellization and adsorption of the prepared surfactants,[12] which indicate that the prepared surfactants based

on R-EO9, ERID-1, and ERID-1 favor adsorption at interface than micellization in the bulk solution. This result assumes that the prepared surfactants behave like resins and are coadsorbed onto the micellar core resins. It was also observed that the viscosity was increased with increasing wt % of sludge. The data indicate that the dispersion capability of these dispersants decreases as the viscosity increases. It can be concluded that the diffusion of the dispersant to the highly viscous oil phase requires more energy.

CONCLUSIONS

Rosin acids were modified by esterification and amidation reactions to produce water soluble polymeric surfactants. Carboxylic acid group of rosin was esterified with PEG having different molecular weights to produce water soluble surfactants having different HLB. Rosin was reacted (as diene) with MA (as dienophile) in 1,4 Diels–Alder reaction to produce water soluble rosin ester and imide surfactants. The viscosity data indicate that the best ratio between fresh crude oil and sludge is 50 : 50 wt %. The sludge is not soluble in the crude oil without surfactant additives at temperature of treatments (60°C), while the solubility of the sludge into crude oil was enhanced by addition of the prepared surfactants. R-EO9, ERID-1, and ERID-1 show low viscosity values than other surfactants when added to crude oil sludge blends. ERID-1 is more effective as asphaltene stabilizers (good dispersion efficiency), which show low viscosity values than other surfactants when added to crude oil sludge blends.

References

1. Ramos, A. C. S.; Haraguch, L.; Notrispe, F. R.; Loh, W.; Mohamed, R. S. J Pet Sci Eng 2001, 32, 201.
2. Mohamed, R. S.; Loh, W.; Ramos, A. C.; Delgado, C. C.; Almeida, V. R. Pet Sci Technol 1999, 17, 877.
3. Loh, W.; Mohamed, R. S.; Ramos, A. C. S. Pet Sci Technol 1999, 17, 147.
4. Becker, H. L. SPE Permian Basin Oil and Gas Recovery-Conference, 21–23 March, Midland, Texas; Paper No. 59703 (2000).
5. Andersen, S. I.; Speight, J. G. J Pet Sci Eng 1999, 22, 53.
6. Junior, L. C. R.; Ferreira, M. S.; Ramos, A. C. S. J Pet Sci Eng 2006, 51, 26.
7. Gonza Lez, G.; Middea, A. Colloids Surf 1991, 52, 207.
8. Ibrahim, H. H.; Idem, R. O. Energy Fuels 2004, 18, 743.
9. Denoyel, R.; Giordano, F.; Rouquerol, J. J Colloids Surf A Physicochem Eng Asp 1993, 76, 141.
10. Hinze, W. L.; Pramauro, E. Crit Rev Anal Chem 1993, 24, 133.
11. Tuttle, R. N. J Petrol Technol 1983, 35, 1192.
12. Atta, A. M.; Ramadan, A. M.; Shaffei, K. A.; Nassar, A. M.; Ahmed, N. S.; Fekry, M. J Dispers Sci Technol 2009, 30, 1100.
13. Morkhade, D. M.; Nande, V. S.; Barabde, U. V.; Patial, A. T.; Joshi, S. B. AAPS Pharm Sci Technol 2007, 8, 47.
14. Rocha, N. O.; Khalil, C. N.; Goja, A. M. International Symposium on Oil field Chemistry, 28 February-2 March, Houston, Texas, U.S.A.; Paper No. 105765 (2007).
15. Tuttle, R. N. J Petrol Technol 1983, 6, 1192.
16. Heath, G. M.; Heath, R. A.; Dundr, Z. Acta Montanistica Solvaca 2004, 9, 184.
17. Asia, I. O.; Enweani, I. B.; Eguavoen, I. O. Afr J Biotechnol 2006, 5, 461.
18. Pavlova, A.; Ivanova, R. J Environ Monit 2003, 5, 319.
19. Mukherjee, S.; Kushnick, A. P. Symposium on Advanced Oil field Chemistry, Division of Petroleum Chemistry Inc., A.C.S., Toronto, Canada, 205 (1988).
20. Chang, C. L.; Fogler, H. S. Langmuir 1994, 10, 1749.
21. Leon, O.; Rogel, E.; Urbina, A.; Andujar, A.; Lucas, A. Langmuir 1999, 15, 7653.