Characterization of Asphaltenes and Resins Separated from Water-in-Crude Oil Emulsions formed in Kuwaiti Oil Fields

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Abstract

Knowledge of the properties and behavior of asphaltenes and resins is indispensable for the design of preventive and curative measure for emulsion problems created by the presence of asphaltene, resins and other organic and inorganic solids. In order to understand the phenomena of water-oil emulsions formed in Kuwaiti oil fields and determine the factors involved in the stabilization of these emulsions, the role of asphaltenes, resins and wax separated from various samples of oil field emulsions formed in Burgan oil field have been evaluated.

Physicochemical properties of asphaltenes, resins, wax, and de-asphalted de-resined (DADR) oil samples have been studied via FT-IR, ^{1}H and ^{13}C NMR, elemental analysis, and differential scanning calorimetry (DSC). These emulsion samples contain different amount of water ranges from 24 to 35%, asphaltenes content ranges from 0.9 to 1.7%, resins content from3.7 to 4.6%. IR-FT spectra were performed to identify the various functional groups which have an effect on the stability of water-oil emulsions. The freezing behavior of an emulsion was characterized by differential scanning calorimetry to determine whether the water in the emulsion is free water or emulsified water.

Key words: Asphaltenes; Resins; Wax; Water-Oil Emulsions; Functional Groups

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1. Introduction

Great deals of formation water are produced simultaneously with crude oil in many wells and its amount increases proportionally with the production history of the oil field (Kokal and Al-Ghamdi, 2005). About 80% of exploited crude oils exits in an emulsion state, all over the world. The more common emulsions in the petroleum industry are of the water-in-oil (W/O) type (Xia et al, 2004). Some of the produced water can settle very quickly as free water while the rest remains in the oil as small droplets suspended in continuous oil phase. The suspended water is forming water-oil emulsion. Emulsions formed due to the presence of water associated with oil production and the intense mixing of water with oil as it is lifted in the wellhead and as it passes through chocks valves. This mixing creates high shear stress and lead to very stable water in oil emulsions. Some of the emulsions are very hard to break or treat and some cause costly operational difficulties such as: tripping of the equipment in wet crude handling and facilities, excessive pressure drop in flow lines due to increased viscosity of the emulsion, and sever corrosion of refinery equipments because the water usually carry dissolved salts (Yan et al., 1999; Hu and Guo, 2001; Ramos et al., 2001; Evdokimov et al., 2003; Mousavi-Dehghani et al., 2004; El Gamal et al, 2005). Asphaltene precipitation and subsequent formation of tight emulsion at producing sand face have also been attributed to productivity decline in many producing oil wells (Kokal et al., 2003).

Kokal and Wingrove (2000) presented three case studies dealing with problems of emulsion created in oil fields. In the first case, Ghawar oil field- the largest oil field in the world, problems arose with plant upset in some wells and increase use of demulsifier to break the emulsion. The emulsion problem was linked to the precipitation of organic and inorganic scales during crude oil production. The second case, the Zuluf offshore oil field, where the problem is related to heavy emulsion sludge deposition in the de-sanders at the offshore gas oil separation plant. The third case is for large offshore (Berri) oil field which is producing from several reservoirs including low API gravity and highly viscous crudes. Initial study highlighted that the more viscous crudes and asphaltenes from these reservoirs were responsible for the tight emulsion observed in Berri. Electric shorting due to increased water in the desalters was encountered in Berri field in addition to equipment tripping and consumption of great amount of demulsifier. Produced oil-field emulsions are classified in term of its stability as measured by the amount of water that will settle from oil after a given time. Three types of emulsions are encountered in oil fields: loose, medium, and tight. Loose emulsions are defined as ones where water separates from oil very quickly in a matte of few minutes as free water. Medium emulsions where water will separate in matters of tens of minutes. Tight emulsions are ones where water will partially separate from crude oil in matters of hours, days or even weeks, (Kokal, 2002). The viscous emulsion will foul machinery and entrained solids associated with stable emulsion will accumulate in certain cases plug process equipment. Thus the process of emulsion breaking can be looked at as a kinetically controlled process, which is enhanced by several competing variables. To devise effective treatment of these emulsions, it is necessary to understand how they are stabilized (Gafonova and Yarranton, 2001).

Organic and inorganic solids stabilize water-oil emulsions (Sarbar and Wingroove; 1997). These solids mainly consist of clay minerals, asphaltenes, resins, and wax. These particles, such as clay and wax adsorb the polar constituents of oil resulting in modification of its wettability, allowing them to be placed at the water-oil interface and contribute to emulsion stability (Kim et al., 1990; Mc Lean and Kilpatrick, 1997a,b). Particles and surfactant in crude oils can act as emulsifying agents and thus promote and stabilize water-oil emulsions (Bora, 1991).

Asphaltenes precipitation from crude oils under unfavorable conditions causes many problems. When they precipitate downhole, asphaltenes can result in restriction in flow in the vicinity of the wellbore or cause formation damage depending on where they are formed. Even after oil is produced to the surface, the asphaltenes continue to cause problems in the following ways: (1) by stabilizing the water - oil emulsions, (2) by collecting at the oil-water interface of oil-water separators and forming a rag layer that interfaces with the operation of the separator and make oil-water separation difficult, (3) by deposition in the separator and lowering their fluid capacity, therefore reducing the residential time of processing fluids, and (4) by falling to the bottom of separators, contaminating discharge water, and subsequently, causing formation damage in the disposal wells. (Khadim and Sarbar, 1999).

The degree to which solids increases emulsion stability depends on several factors such as particle size, shape and morphology, density, concentration and surface coverage, and wettability (Gelot, et al., 1984; Yan et al., 1999, 2001; Tambe and Sharma,1993, 1994; Aveyard, et al., 2003). Sztukowski and Yarranton (2004) investigated the role of solids in the stability of oil filed emulsions. They found that emulsion stabilized by fine solids and asphaltenes were most stable at a 2:1 fraction area ratio of asphaltene to solids.

A number of studies have demonstrated the importance of asphaltenes, resins, and wax in promoting and stabilizing water-oil emulsions (Yarranton et al., 2000; Khristov. et. al. 2000). Kokal (2002) studied several factors causing the formation of emulsion in oil fields and found that there is a strong correlation of asphaltene content of crude oil with emulsion tightness. Ebeltoft et al. (1992) found that removal of asphaltenes from crude oils produces very unstable emulsions and when wax and asphaltenes were added back to de-asphalted oil, a stable water-oil emulsion was formed. The stability of water-oil emulsion depends also on the total structure of the molecular matrix of the interfacially active components. Size, aromaticity, type of carbonyl functionality, and other functional groups play important role in the stability of the emulsions (Li et al, 2002). With the increasing energy demand and current level of oil prices, applications of enhanced oil recovery become inevitable. Therefore, the study of the behavior of asphaltenes and resins found in crude oils and through understanding of their complex aggregation/deposition processes are fundamental for the formation of production programs and development of inhibitors and dispersants to avoid and/or minimize production losses caused by asphaltene deposition and formation of emulsions (Ramos et al, 2001).

2. Experimental

2.1 Separation of asphaltene and resins from crude oils

Crude oils were shaken overnight to ensure homogeneity of each sample. Normal heptane was added later to crude oil in 10:1 volume ratio to precipitate asphaltenes. The crude oil heptane mixture was keep overnight before asphaltenes was separated. Asphaltenes were removed later by vacuum-filtration. The separated asphaltene was washed with excess n-heptane, and further washing was done by Soxhlet extractor with n-heptane to remove residual resins that might be adsorbed on asphaltene. Asphaltene was obtained by Soxhlet extraction with toluene leaving sediment in the extraction thumb. Finally, toluene was then removed by evaporation under reduced pressure and dried at 60 ˚C overnight to give pure solid free and free-flowing asphaltene.

The n-heptane filtrates containing de-asphalted oil were mixed with silica until a viscous mass is formed. Silica was removed later by filtration and washed with excess n-heptane until colorless solvent drops are passing through. A mixture of benzene-methanol (in 90:10 volume ratio) was used to desorb resins, which was obtained by evaporating the solvent mixture under reduced pressure and drying at 60 ˚C overnight.

2.2 Separation of wax from crude oils

Crude oil samples were heated to 70 ˚C to ensure complete dissolution of all solid phases. The oil sample was then mixed with pentane in 1 to 40 volume ratio, left overnight, and later filtered to remove asphaltene and other sediments. A given volume of petroleum ether, usually 35 ml, was added to 5 g of sample and stirred until the sample is thoroughly dissolved. A given volume of acetone (10 ml) was added and well stirred. The sample was then kept at -20 ˚C for 2 hours. Buchner porcelain filtering funnel, Whatman No. 934 glass fiber filter, vacuum flask and a mixture of three parts of acetone plus one part of ether were all pre-cooled to -20 ˚C. Before filtering the cold sample /solvent mixture, the filter was seated in the filter funnel by wetting the filter with cold solvent mixture and evacuating the assembled apparatus. The sample was filtered by pouring slowing into the funnel, using stirring rod as a guide. The stirring rode, bottle and filter cake were washed with cold solvent mixture. The vacuum was disconnected;

the filter was removed with forceps, and placed in original tarred bottle, the wax crystals in the filter funnel and stirring rode were washed into the bottle with toluene. Later, toluene was allowed to evaporate to complete dryness and the bottle was re-weighted. The difference between the tar and the final weight, less the weight of filter used, is the weight of wax crystal contained in the original 5 g sample.

2.3 Liquid state ^1H and ^{13}C NMR

Liquid state ^{1}H and ^{13}C NMR were carried out for asphaltene and resins on Bruker Avances 400 spectrometer. The apparatus is operating at ^{1}H resonance frequency of 400 MHz and ^{13}C resonance frequency of 100 MHz. ^{1}NMR spectra were obtained with a plus width of 2.67 µs, recycle delay of 5 sec, data point of 8K, tube diameter of 5 mm, spectral width of 18 ppm , and at least 200 scans. ^{13}C NMR spectra were obtained with plus width of 2.27 µs (30° flip angle) data point 8 K, tube diameter of 5 mm, solvent $CDCL^3$ spectral width 250 mm, recycle delay of 2 sec and nearly 20,000 scans.

2.4 Infrared analysis

Infrared spectra were recorded on Perkin Elmer system 2000 (FT-IR) spectrometer in absorbance and transmittance mode for oil, asphaltene, and resins. Each spectrum resulted from the accumulation of 100 scans with spectral resolution of 4 cm in the 400 cm^{-1} spectral domain. Samples were prepared by mixing with spectroscopic grade KBr. Spectra were acquired relative to a pure KBr reference.

2.5 Elemental analysis

Elemental analysis was carried out for oils, asphaltenes, resins and DADR oil samples using Leco Chns-932 elemental analyzer. The instrument was first calibrated with a suitable standard such as sulfamethazine and acetanilide as recommended by ASTM D5291 method. From elemental analysis; carbon, hydrogen, nitrogen, and sulfur content of each sample was determined.

2.6 Molar mass

Relative molar mass, molecular weight, was measured for oils, asphaltene, resins, and DADR oil samples. Knowledge of molar mass is required for the application of a number of correlative methods that are useful in determining the gross composition of heavier fractions of petroleum. The measurements were carried out by KNAUER vapor pressure osmometer (VPO) which was calibrated with benzyl using chloroform as a solvent.

2.7 Density

PAAR density meter DMA 48 was used to carry out density measurements. The apparatus was calibrated with air and water at ambient temperature. To calculate the density of asphaltene sample, different weights of asphaltene were dissolved in toluene. A graphical relationship between mass fraction of asphaltene in toluene and specific volume was established. The densities of asphaltenes and resins samples were calculated from this relationship.

2.8 Differential scanning calorimetry (DSC) measurements

In the present study, A Mettler Toledo TA 4000 DSC instrument was adjusted to both temperature and heat flow using pure Indium. A series of high purity normal paraffins were also used for low temperature adjustment of the DSC in the temperature range of 50 to -95°C. These materials were chosen because they have known melting temperature and enthalpy of fusion (Elsharkawy et. al., 2000). Published data for melting temperature and enthalpy for Indium were used to program the DSC to draw the baseline. Differences in melting temperature and enthalpy of fusion for normal alkanes between literature data and measured ones were of the order of 0.3 to -4.16°C and 15.88 to 2.4 j/g, respectively. To distinguish free from demulsified water, a series of DSC measurements have been made in the temperature range of 30 to -140°C.

3. Results and discussion

Table (1) reports measurements of weight percent asphaltenes and weight percent resins in emulsion samples, density of emulsion, asphaltene to resins ratio (A/R), and volume ratio of water and sediments. The values for asphaltenes and resins content in the four sample understudy lie within a narrow range. Sample BG 185 has the lowest water and sediment content. It also has the lowest resin to asphaltene ratio, 2.78. This might cause low emulsion stability. Figure (1) shows that there is a linear relationship between density of emulsion and water and sediment content. As the amount of water and sediments in emulsion increases, the density of emulsion found to increase.

Xia et al., 2004 found that emulsion stability was related to the asphaltene and resins in the crude oil. Analysis of asphaltene and water content separated from various emulsion formed in BG oil field are reported in Table (1). These results, plotted in figure (2), show that there is no direct relationship between asphaltene content and amounted of water and sediments content separated from stable emulsion.

Table (2) reports molar mass, density, and elemental analysis of asphaltenes and resins separated from emulsion samples. Due to the narrow range of molecular weight of asphaltenes and resins, the density range is small. As the hydrogen content in the asphaltene and resins increases, the HC ratio increases. This might leads to high percentage of cycloalkanes and aliphatic chains in both asphaltenes and resins. This table also illustrates that the H/S ratio in the resin ranges from 1.54 to 1.72, while the H/S ratio in the asphaltenes ranges from 1.12 to 1.16. This indicates that sulfur in the asphaltene is present as –C-S-C- or fused in cycloalkanes rings rather than HS group while in the resins considerable amount of sulfur is present as HS group. The H/C ratio in resins is higher than that in asphaltenes. Therefore, resins contain less aromatic hydrogen while asphaltene contain high aromatic hydrogen. Table (2) also shows that the molecular weight of the asphaltenes is higher than the molecular weight of resins for all the samples considered in this study. These are in agreement with the molecular weights of asphaltene and resins reported by Mohammed et al, 1996. The results reported in table (2) also shows that asphaltene sample separated from emulsion for a given well has lower hydrogen content than resins sample from the same well. There is no major difference in the nitrogen content between asphaltenes and resins. The sulfur and oxygen content of asphaltene samples is higher than that for resin samples. Similar results were reported by Khadim and Sarbar, 1999. Figure (3) shows that the hydrogen content in the asphaltene is a strong function of the H/C ratio. The data given in table (2) could not establish a general trend for resins.

Characterization of oil samples after the removal of water and sediments from emulsions are given in Table (3). This table shows that these oil samples have narrow range of macular weight and density. It also indicates that the H/C ratio is high as compared with asphaltenes and resins. Therefore, it has less content of aromatic hydrogen and high content of aliphatic hydrogen. When compared with other samples, oil separated from emulsion BG185T contains less water and sediments (24 V/V), has low R/A ratio, low density and high asphaltene content.

Table (4) reports properties of de-asphaltene de-resin oil fraction (DADR oil) separated from emulsion samples after water and sediments have been separated. All DADR oil samples contain high H/C ratio, less aromatic hydrogen and high percentage of aliphatic hydrogen. This is due to separation of the heaviest fractions of asphaltene and resins from emulsion. They also have narrow ranges of molecular weight and density. These oils have almost no nitrogen content, which indicates that all the nitrogen content of the crude oil is present in asphaltene and resin part of each sample. On the other hand, DADR oil samples contain low sulfur content, and high carbon and hydrogen content comparable to that found in asphaltenes and resins. Figure 4 shows that the density of emulsion sample could be expressed as a liner function of the amount of oil contained in the sample.

Table (5) shows DSC results for the four emulsion samples. The freezing behavior of an emulsion can be characterized by differential scanning calorimetry (DSC). The free water freezes at approximately 0°C. Emulsified water super-cools and freezes at lower temperature, depending upon size distribution. The smallest droplets freezes last because of their volume, and fewer nucleation sites are available for ice crystal formation and water freezing. The different freezing behavior of free versus emulsified water gives this technique the potential to quantify relative proportions of these two types of water. The DSC curves show that all emulsion samples have no free water, and that all water is emulsified. These DSC curves show that the emulsified water was separated from the emulsions in the temperature range of -54 to -57°C. The emulsified water is present in the emulsions as tiny droplet in the oil stabilized by asphaltenes, resins and in organic sediments. Hence, the freezing point of this water is drastically shifted from the normal freezing point of free water to -57°C. Figure 5 shows that there is a strong correlation between the amount of water separated from emulsion sample and its freezing temperature.

Table (6) reports IR spectra region assignments for free oils, asphaltene, and resins. It can be concluded from this table that asphaltene resins and oils contain band of variable intensities in the following regions: OH and NH regions (3600-3300 cm^{-1}), C=O region (1800-1600 cm^{-1}), -CH, $-CH_2$ and $–CH_3$ stretching regions (3000-2800 cm^{-1}) and bending region (1450-1375 cm^{-1}), -C-S, C-O, C-N stretching regions (~ 1000 cm^{-1}), aromatic C-H bending region (900-700 cm^{-1}). The SH stretching bands of the variable intensities at around 2500 cm^{-1}. This appears as a weak bond in the following oils: 47T, 185T, and 336T. The stretching band also appears in asphaltene separated from emulsion BG47T only. It also appears in resins BG47T and BG336T. Table (6) also shows that the absence of bands of C=O in all free oils and asphaltenes which means that oxygen in both oils and asphaltenes present as C-O or fused in cycloalkanes rings. However, in resins some oxygen is present as C=O, because the resins contain a weak bond at (1660-1620 cm^{-1}). Free oils, asphaltene, and resins, which have no bands of SH at about 2500 cm^{-1} and have sulfur content, their sulfur might be present as thioether, thiophene rings or other –C-S-C structure.

Table (7) reports the measurements of aliphatic and aromatic hydrogen present in asphaltene (BG336T) and resins (BG321T). It appears that asphaltene which is separated from emulsion sample BG336T with low H/C ratio contains high percentage of aromatic hydrogen (H_{ar}) while resin separated from emulsion sample BG321T with high ratio of H/C contains low percent of aromatic hydrogen.

4. Summary and conclusion

In order to understand the phenomena of water in oil emulsions and determine the factors involved in the stabilization of these emulsions, especially the effect of asphaltene and resins, physical and chemical properties of emulsions as well as asphaltene, resins and wax are measured. Emulsion samples were collected from Burgan oil filed, the largest oil filed in Kuwait and the second largest in the world. These samples are BG47T, BG185T, BG321T, BG33GT, BG366T, and RA4. The physical properties of each emulsion sample such as density, water and sediments contents have been measured by ASTM methods. Compositional properties for various asphaltenes and resins separated from crude oil emulsion formed in Burgan oil filed have been measured. These measurements include molar mass by vapor pressure osmometry (VPO), density, elemental analysis, IR spectra, and ^{1}H-NMR. De-asphalted de-resin oil samples (DADR) were also characterized by measuring molar mass by VPO, density, and elemental analysis.

Asphaltene content in each emulsion sample have also been measured. These samples have asphaltene content ranges from 0.9 to 1.07%. These asphaltene separated from crude oil samples have a molecular weight ranges from 3997 to 4423 and density from 1.22 to 1.25g/cc. The average molecular weights of asphaltenes measured by VPO are within the range of reported values in the literature obtained using VPO as well as Gel Permeation Chromatography (Acevedo et al, 1992; Singh et al, 1993; Ramos et al, 2001).

Elemental analysis of these asphaltene samples indicates carbon content of 76 to 79%, hydrogen content of 7.4 to 7.7%, nitrogen content of 1.16 to 1.25% and sulfur content of 6.4 to 6.6%. Resins in emulsion samples ranges from 3.7 to 4.6%. Elemental analysis of resins samples indicates carbon content of 79 to 81%, hydrogen content of 9.1 to 9.25%, nitrogen content of 1.14 to 1.18% and sulfur content of 5.2 to 6%. The resin/asphaltene ratio in the emulsion samples ranges from 2.8 to 4.4. The water and sediments content in the emulsion samples were also measured, by ASTM D4007, and found to range from 24 to 35%. To distinguish fee water from emulsified water in each sample, differential scanning calorimetry (DSC) measurements have been carried out. These measurements show that the samples have no free water and that the emulsified water super-cool at temperature ranging from -54 to -57 °C. These measurements indicate that solids have an important role in stabilization of water in emulsion. IR Fourier transform infrared (FT-IR) spectra were performed in the transmission and adsorption modes. The IR transmission spectra show medium content of OH and NH groups for oil part of the sample, high content in asphaltene, and resins aggregation through hydrogen boning. The IR spectra of oil samples shows weak bonds of SH group at about 2400 cm^{-1} and high H/S ratio ranges from 4 to 4.45. This indicates that sulfur is found in oil as SH group. The IR spectra of asphaltene samples shows weak bond for SH group at 2400 cm^{-1} at H/H ratio ranges from 1.12 to 1.16. The sulfur content in asphaltene, therefore, is probably of the fused ring type or as –C-S-C and small amount of sulfur is found as SH groups. Elemental analysis of resins samples shows H/S ratio ranging from 1.54 to 1.72. Most of the sulfur content is found as fused rings and small amounts as SH groups. The elemental analysis also shows that HS ratios in oils are greater than that in asphaltenes. This may be due to the presence of S and H as SH groups between condensed rings in oil and fused in ring in asphaltene and resins. Thus, the probability of the presence of sulfur as –C-S-C or fused in condensed rings increases.

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Table (1) Characteristics of emulsion samples.

Emulsion sample	Wt.% A in emulsion	Wt.% R in emulsion	Emulsion density @20˚C	R/A ratio in emulsion	Sediment& water in emulsion* (V/V)
BG47T	0.9185	3.8620	0.9370	4.205	30
BG185T	1.6596	4.6180	0.9270	2.783	24
BG321T	1.2225	3.6990	0.9453	3.026	35
BG366T	1.0045	4.3935	0.9444	4.374	35
BG75	1.4201	17.6	0.9250	12.394	28
RA4	2.8100	19.6	0.9750	8.991	34

A	Asphaltene
R	Resins
*	ASTM 4007

Table (2) Characterization of Asphaltenes (A) and resins (R) separated from emulsions formed in BG Oil fields.

							Elemental analysis				
sample	Wt% (A&R) in emulsion	Wt% (A&R) in oil	Molar mass	Density @20˚C	H/S ratio	H/C ratio	C%	H%	N%	S%	O%
A47T	0.9185	1.3121	4246	1.2374	1.1630	1.1623	76.50	7.463	1.159	6.41	8.454
A185T	1.6595	2.1836	4052	1.2415	1.1498	1.1487	76.66	7.391	1.221	6.42	8.295
A321T	1.2225	1.8808	4432	1.2256	1.1197	1.1706	78.67	7.729	1.233	6.91	5.460
A366T	1.0045	1.5454	3997	1.2430	1.1324	1.1541	76.85	7.443	1.255	6.57	7.883
R47T	3.8620	5.5171	1150	1.1047	1.7208	1.3684	79.22	9.098	1.143	5.29	5.251
R185T	4.6180	6.0763	984	1.0859	1.6387	1.3629	79.36	9.077	1.167	5.54	4.856
R321T	3.6990	5.6908	1121	1.1099	1.5628	1.3561	90.98	9.216	1.156	5.89	2.753
R366T	4.3935	6.7592	992	1.0860	1.5407	1.3595	81.09	9.252	1.181	6.05	2.468

Table (3) Characterization of crude oil separated from emulsions formed in BG Oil fields.

sample	Wt% A	Molar mass	Density @20◦C	H/S ratio	H/C ratio	Elemental analysis				
						C%	H%	N%	S%	O%
47T	1.312	399	0.9294	4.1497	1.6556	82.645	11.483	0.0669	2.7672	3.0379
185T	2.184	392	0.9255	4.4565	1.7038	83.026	11.872	0.1043	2.6640	2.3337
321T	1.881	395	0.9203	3.9984	1.6231	80.594	10.978	0.1006	2.7456	5.5818
366T	1.545	403	0.9383	4.1173	1.6243	81.714	11.139	0.0705	2.7054	4.3711

Table (4) Characterization of De-asphalted de-resin oil fraction of emulsion samples.

sample	Wt% in emulsion	Molar mass	Density @20◦C	H/S ratio	H/C ratio	Elemental analysis				
						C%	H%	N%	S%	O%
47T	45.9665	375	0.9232	4.3368	1.664	84.054	11.755	0.0000	2.7105	1.4805
185T	50.0650	378	0.9207	4.4530	1.6638	84.150	11.750	0.0266	2.6387	1.4347
321T	43.2570	385	0.9246	4.1345	1.6592	83.864	11.678	0.0603	2.8245	1.5732
366T	43.6705	387	0.9205	4.2691	1.6535	84.154	11.675	0.0187	2.7355	1.4138

Table (5) Differential scanning calorimetry data for various emulsion samples.

Sample	Enthalpy (ΔH), j/g	Emulsified water freezing temperature, ˚C	Water& sediments (V/V)
47T	53.8	-56.2	30
185T	33.5	-57.1	25
321T	48.2	-54.9	35
366T	50.5	-55.6	35

Table (6) Infrared spectra region assignments for oils, asphaltene, and resins separated from emulsions formed in Kuwaiti BG field.

IR band transmission	OH, NH (stretch) (3300-3600)	C-H (stretch)	SH (-2500)	C=O (1660-1800)	C=C stretch (1375-1450)	C-H, CH_3 (1375-1450)	C-S,C-O,C-N (~1000)	C-H (aromatic) (700-900)
Oils								
47T	3384(m), 3187(w)	2925(x)	3262(w)		1603(x)	1463(s),1377(s)	1032(m)	725,760,811,868 (m)
185T	3384(m), 3188(w)	2924(x)	2380(w)		1604(s)	1462(s),1377(s)	1031(m)	694,727,760,811,868
321T	3187(w)	2926(x)	2360(w)		1603(x)	1463(s),1377(s)	1032(m)	694,727,811,868(m)
336T	3383(m), 3183(w)	2927(x)	2335(w)		1605(s)	1463(s),1377(s)	1031(m)	649,728,811,869(m)
Asphaltenes								
47T	3411(s)	2921,2850(x)	2400(w)		1597(m)	1433(s), 1375s)	1029(m)	730,760(w),802(m)
185T	3429(s)	2920,2850(x)			1598(m)	1453(s), 1375s)	1029(w)	748(w),803(w)
321T	3430(s)	2920,2850(x)			1597(m)	1452(s), 1375s)	1029(w)	747, 808,861(w)
336T	3412(s)	2921,2850(x)			1597(m)	1458(s), 1375s)	1029(w)	747,808,860(w)
Resins								
47T	1433(w)	2923,2852(s)	24009w)	1620(w)	1598(w)	1457(s), 1376(s)	1029(m)	725,807,870(w)
185T	3260(w),3400(w)	2924,2852(x)		1640(w)	1597(w)	1458(s), 1376(s)	1023(m)	724,750,811(w)
321T	3433(w)	2923,2852(x)		1640(w)	1803(w)	1458(s), 1376(s)	1029(m)	748,770,820(w)
336T	3422(w)	2923,2852(s)	2362(m)	1660(w)	1602(w)	1457(s), 1376(s)	1021(m)	747,811,870)w)

S	Strong band
M	Medium band
W	Weak band
A	Asphaltenes
R	Resins

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Table (7) hydrogen atoms distribution in asphaltene and resins separated from BG emulsions

sample	H_α	H_β	H_γ	H_{ar}	H/C
A336T	22.07	50.92	17.71	9.30	1.154
R321T	18.11	61.98	17.71	4.85	1.356

A	Asphaltene
R	Resin

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Fig1

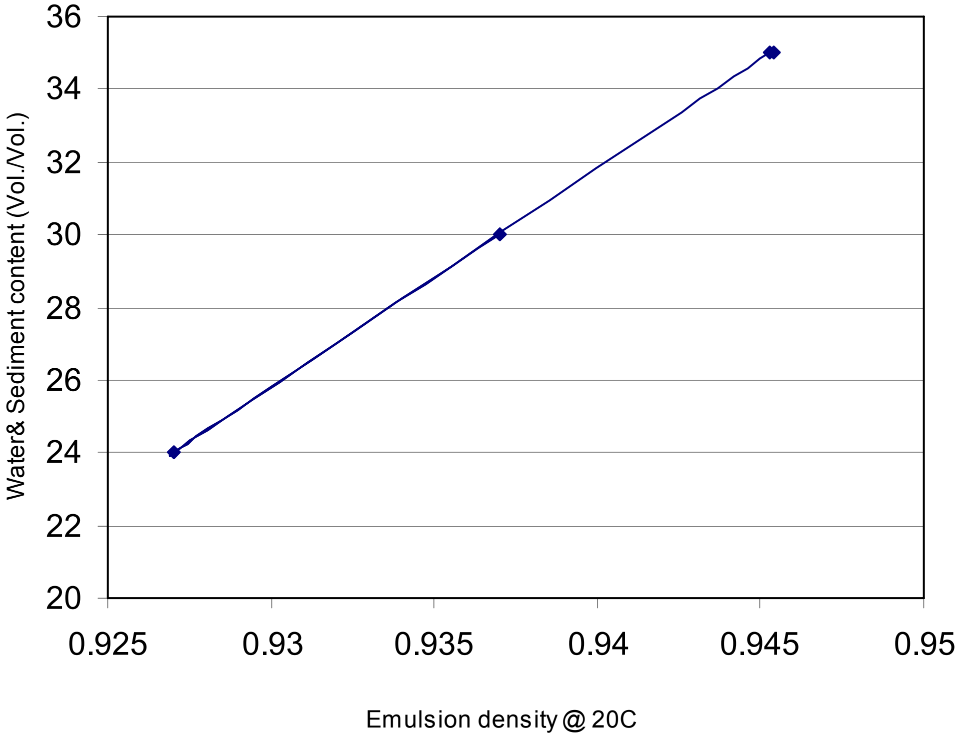

Figure 1- Relation between water and sediment content of emulsions from BG and emulsion density

Fig2

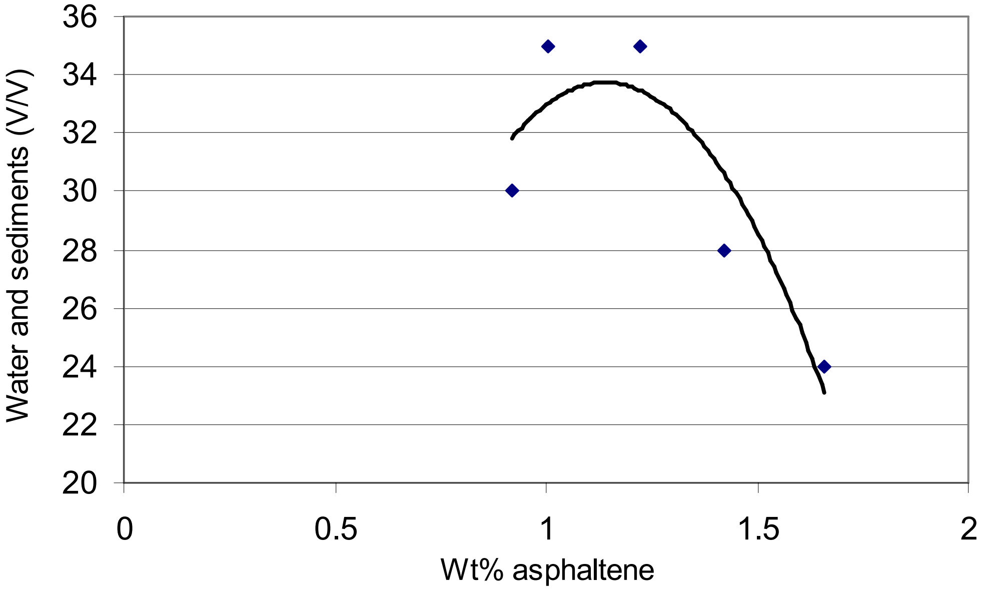

Fig 2- Water and of asphaltene content on emulsion

Fig3

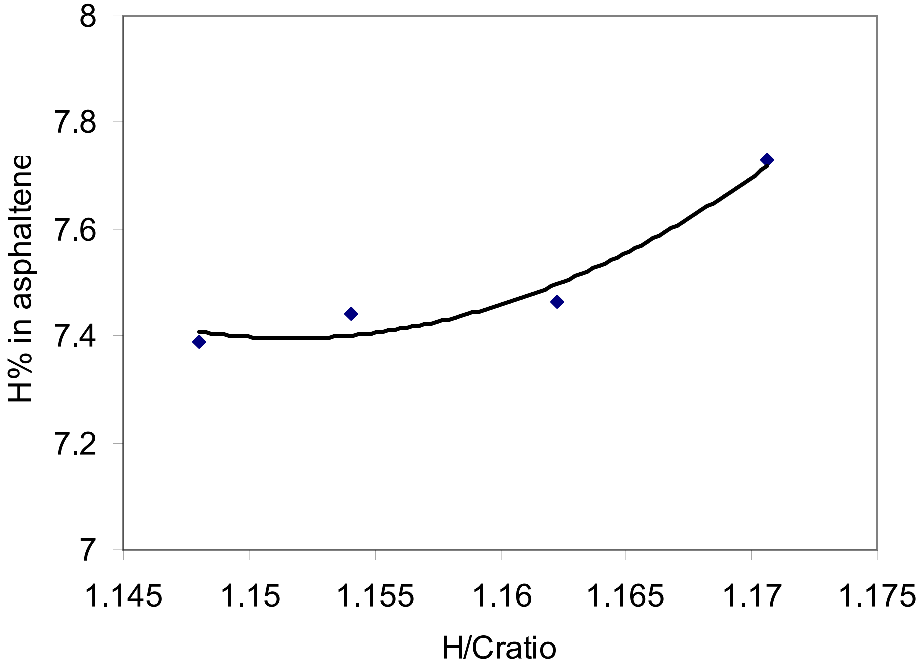

Figure 3- Hydrogen content in asphaltene

Fig4

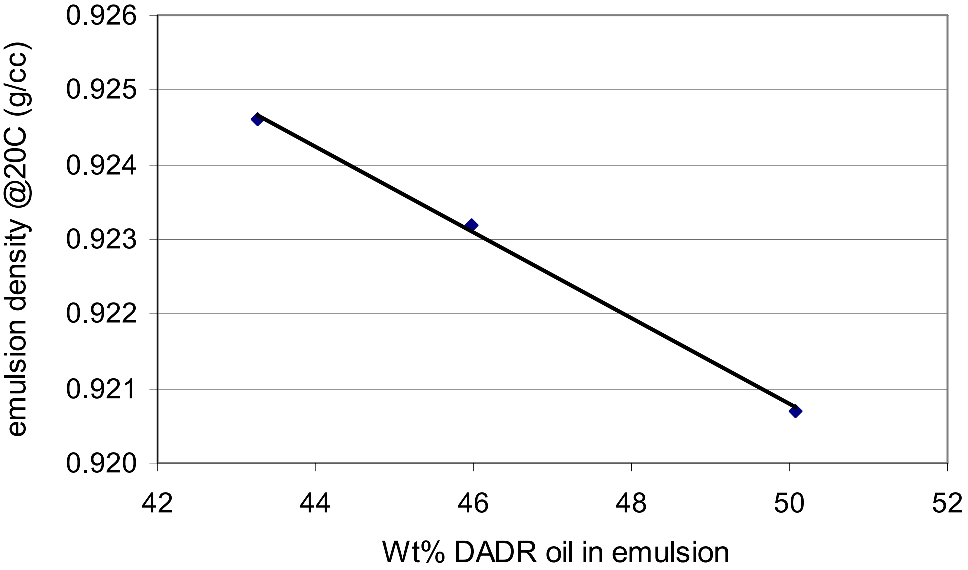

Figure 4- Relatioship beween amount of oil and emulsion density

Fig 5

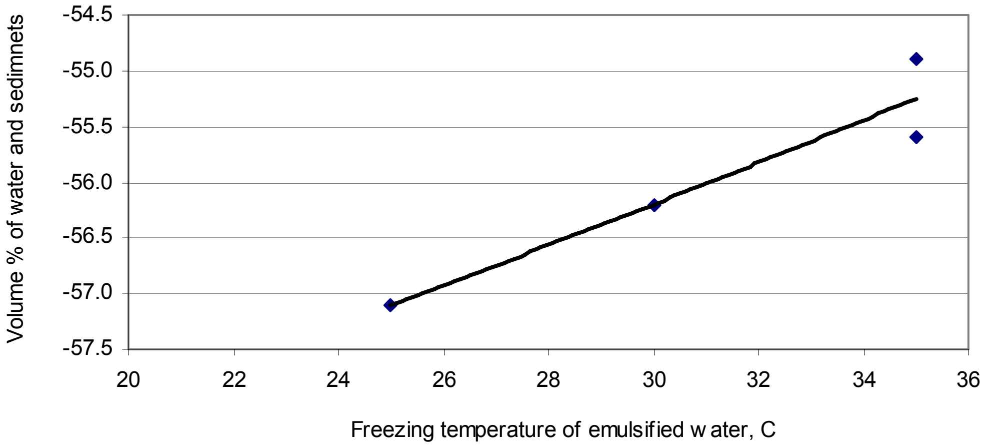

Figure 5- Effect of volume of emulsified w ater on freezing temperature