Final Report

Laboratory-Scale Investigation of a Method for Enhancing the Effectiveness of Oil Dispersants in Destabilizing Water in Oil Emulsions

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Brief Project Description

The primary objective of this project was to investigate the feasibility of enhancing the de-emulsifying properties of commercially-available oil dispersants by modifying the composition and fraction of polar constituents in the oil phase of water-in-oil (W/O) emulsions and increasing the pH of the emulsion aqueous phase.

The general approach envisioned for this project was to select candidate polar additives based on human and ecological toxicity, solubility (in crude oil, water, and dispersant solutions), reactivity in dispersant solutions, and effectiveness in increasing the de-emulsification properties of commercially-available dispersants. Additional properties of interest include the ability to modify dispersant solution pH (or tolerate basic solutions). Experiments were conducted using raw crude oil from the Macondo Prospect well (MC252; Deepwater Horizon accident), the dispersant COREXIT 9500 (Nalco Company), and actual W/O emulsions from the Deepwater Horizon accident collected from coastal Gulf of Mexico waters near Pensacola, Florida by our research team in late June 2010. In addition, standardized W/O emulsions were created following approaches previously reported in the literature, and new approaches developed by our research team as part of this project. Experiments using Texas intermediate crude oil were conducted to optimize laboratory methods for developing stable emulsions and to examine the effectiveness of developed approaches for de-stabilizing W/O emulsions.

Project activities focusing primarily on the chemical characterization of oils used in experiments, acquisition of ancillary information necessary for conducting de-emulsification experiments, methods for creating stable W/O emulsions for use in de-emulsification experiments, and initial results from preliminary de-emulsification experiments were presented and discussed in the interim report (Hayworth, 2012) and are provided in Part 1 of this report. In Part 2 of this report, we present and discuss the results of emulsion destabilization experiments using surrogate emulsions created using surrogate MC252 raw crude oil and actual MC252 emulsions collected and archived by our research team in June, 2010 following the Deepwater Horizon accident.

Project Timeline

A 2-month no-cost extension was approved by BSEE in August 2012. The no-cost extension was requested for two primary reasons: (1) instrument issues in our laboratory that delayed our ability to conduct experiments, and (2) emergency leave for a critical member of our research team. The modified project timeline is given in Table 1.

Table 1. Modified Project Timeline

Event	Month from Start of Project														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Baseline characterization of primary experimental materials															
Crude oil fractionation experiments															
Preliminary/final development of analytical procedures (oil/dispersant)															
Selection of candidate polar and other additives															
Interim Summary Report															
Emulsion destabilization experiments (raw crude oil)															
Raw crude oil with seawater															
Raw crude oil with seawater and dispersant															
Raw crude oil with seawater and modified dispersant															
Emulsion destabilization experiments (DHE)															
Standardized DHE with seawater															
Standardized DHE with seawater and dispersant															
Standardized DHE with seawater and modified dispersant															
Emulsion destabilization experiments using unmodified DHE															
Reporting															
Interim (Summary) Report															
Draft Final Report															
Final Report															
Preparation of Manuscript(s) for Publication in Peer-Reviewed Journal(s)															

Part 1. Project Activities Related to Chemical Characterization of Experimental Oils, Acquisition of Ancillary Information, and Methods for Creating Stable Emulsions

Characterization of Oil

The main types of oil used in this project were (1) MC252 surrogate oil provided by BP through Ohmsett; (2) Texas intermediate oil provided by ONTA, Inc.; (3) MC252 emulsion collected by our research team from Perdido Bay, northern Gulf of Mexico, in June 2010. Basic oil characterization was performed for each oil type. Oil characterization was performed using an Agilent gas chromatograph/quadrupole mass spectrometer (Figure 1). As part of this

Figure 1. Photograph of Agilent 7890A/7000B series GC/QqQ MS system used for chemical analysis of oil samples during this project.

project, our research team developed and validated analytical methods and protocols specifically designed for rapid quantitative analysis of fresh and weathered W/O emulsions. The general approach involved extraction of an oil sample into 40 mL of solvent consisting of hexane: dichloromethane (3:1, v/v). After stabilization (~ 10 minutes), the extracted sample was filtered through a 0.2 µ PTFE membrane filter into a new vial, and 1.0 g of anhydrous sodium sulfate was added and allowed to equilibrate for 2 minutes. The sample was then filtered through a 0.2 µ PTFE membrane filter and further diluted as necessary to remain within the calibration range.

The GC/MS QqQ system used for oil characterization and analysis was an Agilent 7890A series GC coupled with an Agilent 7000B QqQ MS. Oil analysis was performed in MRM (Multiple Reaction Monitoring) and full scan mode. The MRM method offered higher selectivity and sensitivity. The GC was operated in constant pressure mode with helium as the carrier gas,

using 1-methylphenathrene (R_t 9.118 min) as a standard for retention time locking of the method. PAH separation was achieved using a DB-5ms (Agilent Technologies) column (20 m x 180 µm x 0.14 µm). The GC/MS experimental conditions were optimized using a 27 PAH mixture spiked with four internal standards. The initial GC oven temperature (50 ºC, 0.8 min) was ramped to 180 ºC (1 min) at 70 ºC/min; 7 ºC/min to 230 ºC (0 min); 40 ºC/min to 280 ºC (2 min); 10 ºC/min to 300 ºC (4 min); and 335 at 25 ºC/min (3 min); resulting in a 24.45 min total run time. Post-run back-flush was performed for 4 min at 335 ºC. Helium was used as a carrier gas at a flow rate of 0.8 ml/min. The inlet pressure was set to 22.15 psi, temperature of 300 ºC, and injection (1 µL) was performed in the pulsed splitless mode. The mass spectrometer equipped with electron impact ionization (EI) source was tuned and programmed to quantify PAHs in MRM mode. Ion source temperature was maintained at 350 ºC and the quad 1 and quad 2 temperatures were held at 180 ºC. Seven time-segments were programmed to analyze PAHs in oil samples. Full scan MS analysis was performed over a mass range of *m/z* 50-500 under similar conditions. The collision cell was turned off during full scan analysis. Example data (MRM chromatograms) from oil characterization experiments are shown in Figures 2-4. The concentrations of 16 PAHs (EPA priority pollutants) in each experimental oil are shown in Table 2.

Table 2. Concentrations of 16 EPA Priority PAHs in Experimental Oils

PAHs	Concentration (mg/kg)		
	MC252 Surrogate	MC252 Emulsion	Texas Intermediate
Naphthalene	863.50	1.79	217.05
Acenapthylene	34.10	4.70	21.37
Acenapthene	57.50	3.20	49.31
Fluorene	149.50	6.39	68.90
Phenanthrene	295.50	0.00	141.86
Anthracene	0.00	0.00	132.51
Fluoranthene	295.50	6.39	15.50
Pyrene	22.70	14.80	18.87
Benzo(a)anthrance	17.70	10.38	7.05
Chrysene	63.50	60.20	26.67
Benzo(b)fluoranthene	10.00	8.40	0.00
Benzo(k)fluoranthene	9.10	9.00	0.00
Benzo(a)pyrene	3.53	2.52	0.00
Dibenz(a,h)anthracene	2.40	2.56	0.00
Indeno(1,2,3,-cd)pyrene	2.40	2.56	0.00
Benzo(ghi)perylene	6.30	5.49	0.00

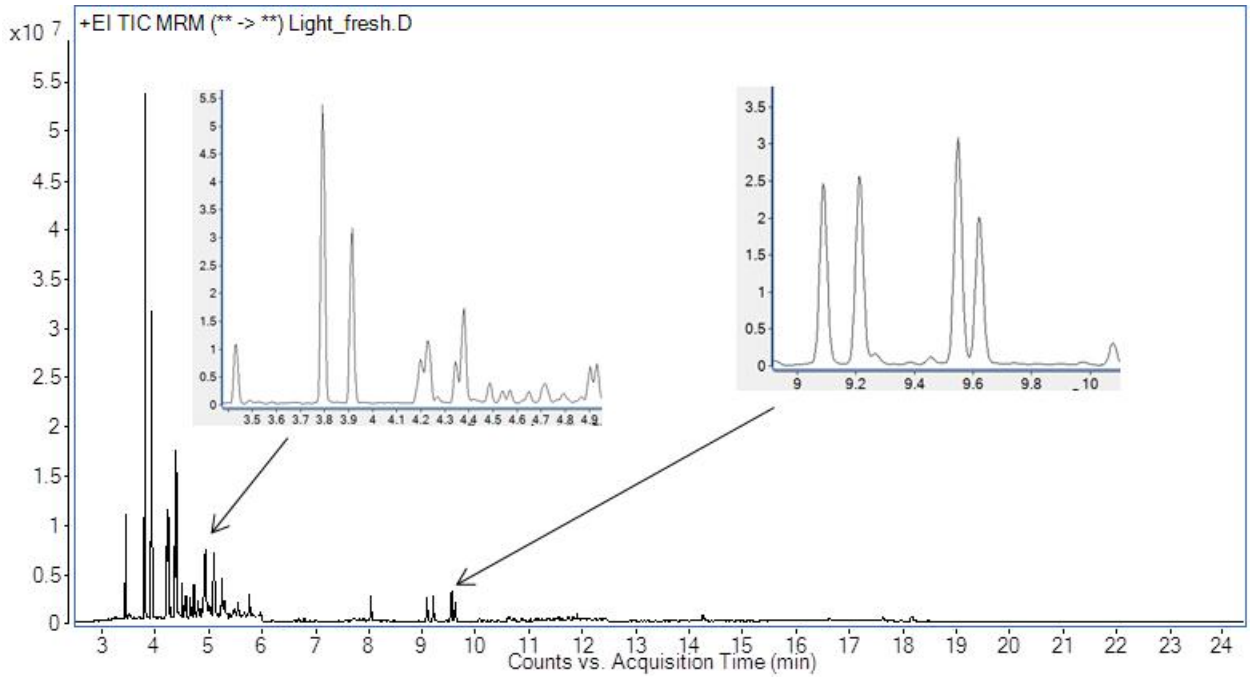

Figure 2. Total ion chromatogram of surrogate MC252 oil by MRM method.

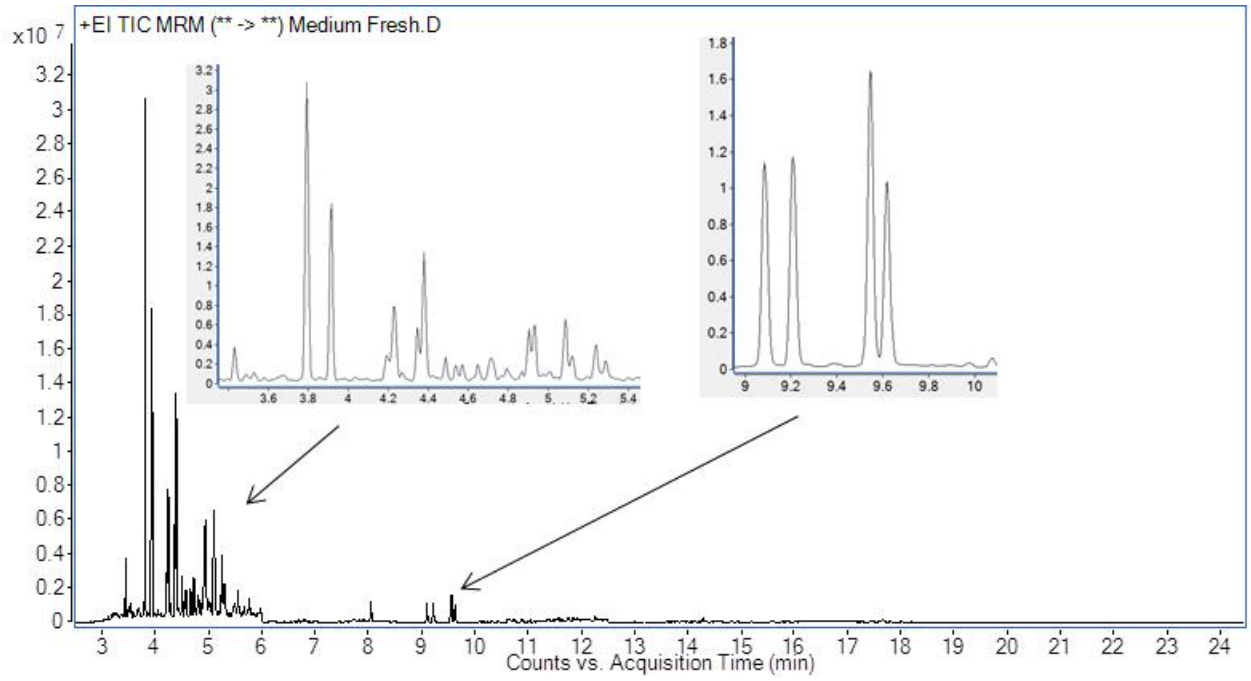

Figure 3. Total ion chromatogram of Texas intermediate oil by MRM method.

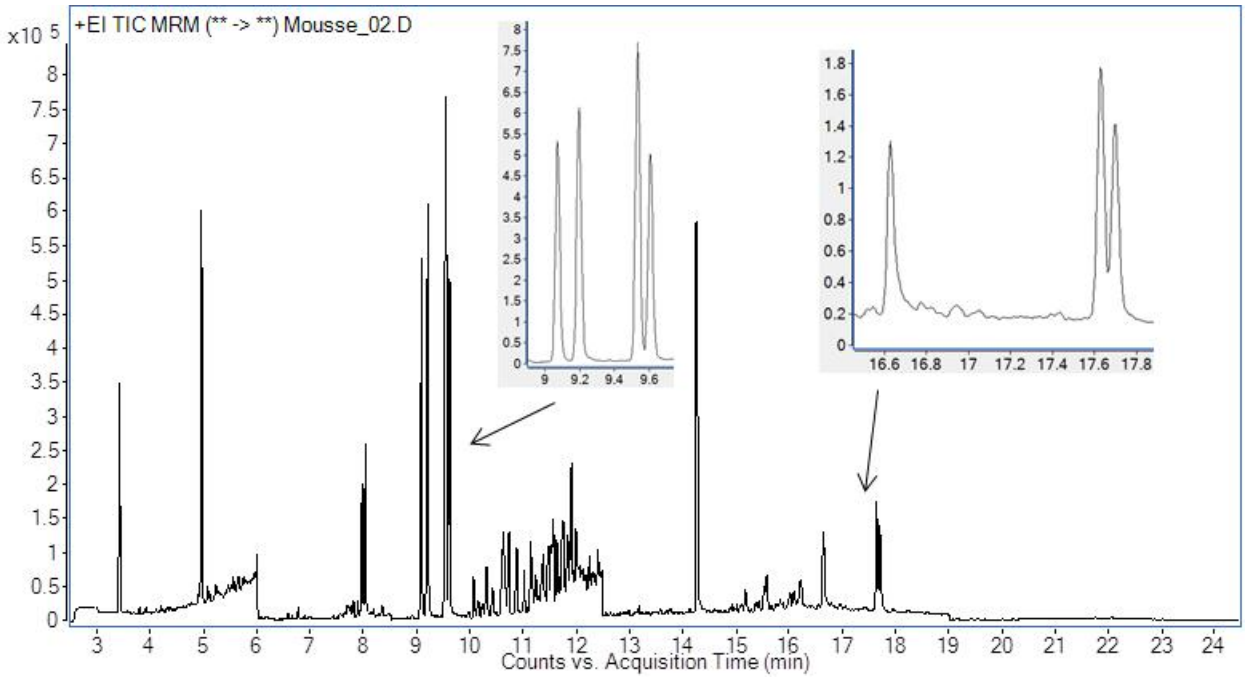

Figure 4. Total ion chromatogram of MC252 emulsified oil by MRM method.

Oil Weathering Experiments

Experiments were performed to create weathered oil samples for assessment of weathering and emulsion formation methodology, using the Texas intermediate oil. Texas intermediate oil was used for these experiments because there were no limitations on the available volume of this oil for the project (as opposed to the limited supply of MC252 surrogate oil and MC252 emulsion). The purpose of the weathering experiments was to simulate the major weathering phenomena of evaporation, dissolution, and photo-oxidation over a relatively short time interval (approximately 25 days); examine the change in polycyclic aromatic hydrocarbon (PAH) concentration in weathered samples over this time period; and validate our method for establishing a chemical baseline for comparison with performance data from de-emulsification experiments. Three weathering scenarios were examined: (1) evaporation, dissolution, and photo-oxidation of raw crude oil under natural conditions; (2) evaporation and photo-oxidation of raw crude oil within a fume hood exposed to broad-spectrum ultraviolet (UV) light; and (3) evaporation, dissolution, and photo-oxidation of raw crude oil (within fume hood exposed to broad-spectrum UV light) during the formation of W/O emulsions.

Oil Evaporation and Photo-Oxidation under Natural Conditions. Experiments to create weathered oil under natural conditions were conducted by placing ~250 mL of Texas intermediate oil into un-covered, 1 L glass beaker and placing outdoors in an area of indirect sunlight. No attempt was made to protect this container from normal weather effects (rainfall); hence, over the course of the experiment approximately 50 mL of water collected within the container. Each day over the course of the experiment, samples were collected and archived for chemical analysis. Samples were collected using disposable glass pipets (4 mL). To collect a sample, the tip of the pipet was placed within the oil phase (overlying aqueous phase accumulated through rainfall), and approximately 2 mL was extracted into the pipet. The sample was transferred into a 4 mL amber glass vial with Teflon-lined screw caps. Samples were stored in a laboratory freezer at 4 °C until analyzed.

Oil Evaporation and Photo-Oxidation within Fume Hood. Experiments to create weathered oil by evaporation under fume hood and exposure to broad-spectrum UV light (photo-oxidation) were conducted by placing ~250 mL of Texas intermediate oil into an un-covered shallow glass evaporation container and placing it in a fume hood equipped with a broad-spectrum UV light source. This container was not exposed to moisture and therefore no aqueous phase was present for oil dissolution. Sample collection, sample frequency, and sample archiving was performed in the same manner as described for the natural conditions experiments.

Oil Evaporation, Dissolution, and Photo-Oxidation during Emulsion Formation. Experiments to create weathered oil emulsions were conducted by placing ~250 mL of Texas intermediate oil into an un-covered shallow glass evaporation container with approximately 500 mL of deionized water. This was placing in a fume hood equipped with a broad-spectrum UV light source. Digital mixers (Caframo Ltd., Ontario, Canada) were used to create the emulsion. Mixing occurred at the interface between the aqueous and oil phase, and was set at a constant rate determined by trial and error to be the most effective at creating an emulsion (~78 rpm). Sample collection, sample frequency, and sample archiving was performed in the same manner as described for the natural conditions experiments.

Summary of Weathered Oil Experiments. Figure 5 shows GC/MS MRM chromatograms for fresh (unweathered) oil, and emulsified oil sampled on day four and day ten of the emulsion weathering experiment. Similar chromatograms were generated for medium oil weathered naturally and weathered under the hood; however, the degree of weathering compared to fresh medium oil for these scenarios was not as pronounced as that for emulsified oil. This is attributed to the relatively short period of time over which weathering occurred for these scenarios, the lack of mechanical mixing (compared to the emulsion scenario), and the lack of dissolution of oil constituents into aqueous solution. Figure 6 shows the full scan GC/MS chromatograms for the same medium oil shown in Figure 5, illustrating the change in analyte mass for a range of oil constituents besides PAHs, as a function of time since the onset of the emulsion weathering experiment. Taking Figures 5 and 6 together demonstrates the effectiveness of the emulsion weathering approach for the medium crude oil. Table 3 shows PAH quantitation for the standard 27 PAHs in the medium crude oil examined in this study. This table illustrates the degree of weathering (based on PAH constituent concentration) relative to the weathering scenarios and time since the onset of the weathering experiments. The point made earlier with respect to the degree of weathering for each weathering scenario is apparent from these data. The emulsion data from Table 3 are plotted in Figure 7 and further illustrate the change in PAH constituent chemistry as a function of weathering time for emulsion weathering experiments.

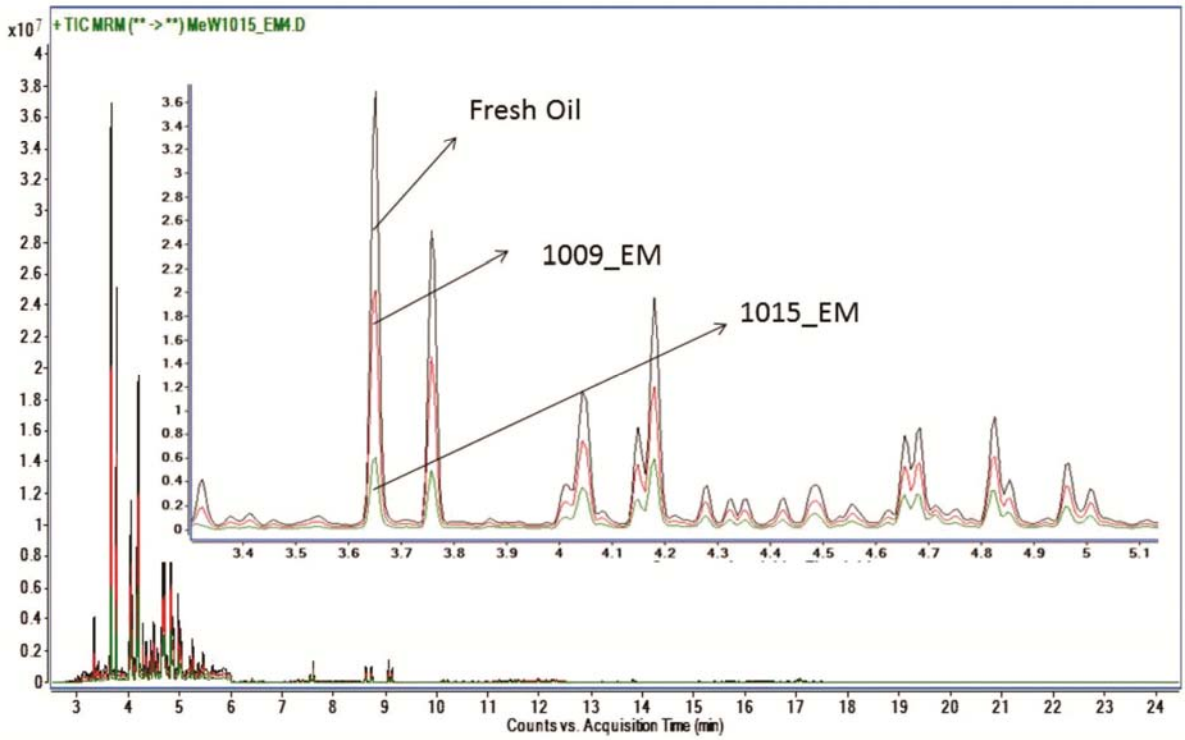

Figure 5. GC/MS MRM chromatograms of fresh Texas intermediate oil (Fresh Oil) verses emulsion on day 4 (1009_EM) and day 10 (1015_EM) of emulsion weathering experiment.

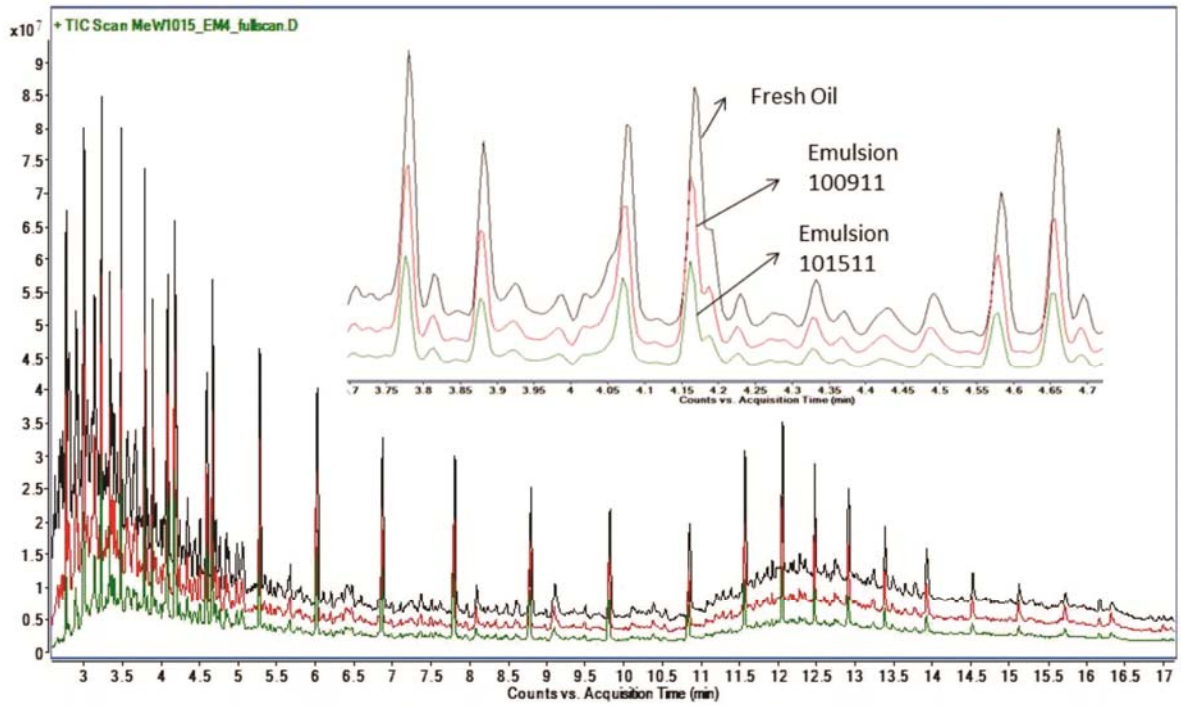

Figure 6. Full-scan GC/MS chromatograms for fresh Texas intermediate oil (Fresh Oil) verses emulsion on day 4 (1009_EM) and day 10 (1015_EM) of emulsion weathering experiment.

Table 3. PAH Quantitation for Texas Intermediate Crude Oil (Un-Weathered and Weathered)

PAHs	Medium Fresh Oil	IM_1009	OM_1009	EM_1009	IM_1015	OM_1015	EM_1015
Naphthalene	217.0475978	186.0733	167.7405	89.3059	143.3280	110.8428	15.4582
1-methylnaphthalene	970.8608	935.0576	901.7110	525.1480	855.1807	741.6580	166.3930
2-methylnaphthalene	629.7398	615.0072	593.4605	350.5018	570.1376	497.7532	124.4757
Biphenyl	91.9361	96.7937	91.1153	57.7278	91.3825	83.2265	29.2760
2,6-dimethylnaphthalene	692.27805	723.3641	696.9676	432.2976	684.2750	610.9879	199.5178
Acenapthylene	21.3679	75.2991	21.1896	15.1921	21.2032	19.7527	28.2284
Acenapthene	49.3066	51.1150	50.6129	32.5295	50.9847	46.7000	19.8649
2,3,5-trimethylnaphthalene	311.4049	347.7708	321.6839	205.1711	334.7238	302.3872	114.5027
Fluorene	68.8976	73.0650	70.4382	46.2324	71.4910	64.7852	27.0573
Dibenzothiophene	15.1108	15.2794	15.3174	11.7115	15.4252	14.7561	9.0147
Phenanthrene	141.8600	142.7274	138.7115	89.4401	146.6378	129.0696	53.1532
Anthracene	132.5136	135.6891	131.6856	85.4495	139.3341	122.3529	49.9903
1-methylphenanthrene	96.9747	110.3332	97.2656	67.0855	101.5059	92.2163	41.2479
Fluoranthene	15.4978	15.5108	15.6777	14.5072	15.7457	15.6391	13.2007
Pyrene	18.8720	19.5105	19.2350	16.2089	19.2159	18.9237	13.8686
Benzo(a)anthrance	7.0516	7.5352	7.3738	6.4461	7.4466	7.3183	14.5896
Chrysene	26.6679	29.1436	26.1975	19.0091	26.8400	25.1293	13.3785
Benzo(b)fluoranthene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Benzo(k)fluoranthene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Benzo(j)fluoranthene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Benzo(e)pyrene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Benzo(a)pyrene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Perylene	5.4968	5.9549	6.1957	5.1724	5.6556	5.5777	4.8567
Dibenz(a,c)anthracene	14.3648	14.1123	14.6237	14.5196	14.7327	14.8190	13.6400
Dibenz(a,h)anthracene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Indeno(1,2,3,-cd)pyrene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Benzo(ghi)perylene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

IM: intermediate oil evaporation and photo-oxidation within fume hood; OM: intermediate oil evaporation and photo-oxidation under natural conditions; EM: intermediate oil evaporation, dissolution, and photo-oxidation during emulsion formation.

1009: Oct. 10, 2011 (fourth day after start of emulsion weathering experiment); 1015: Oct. 15, 2011 (tenth day after start of emulsion weathering experiment).

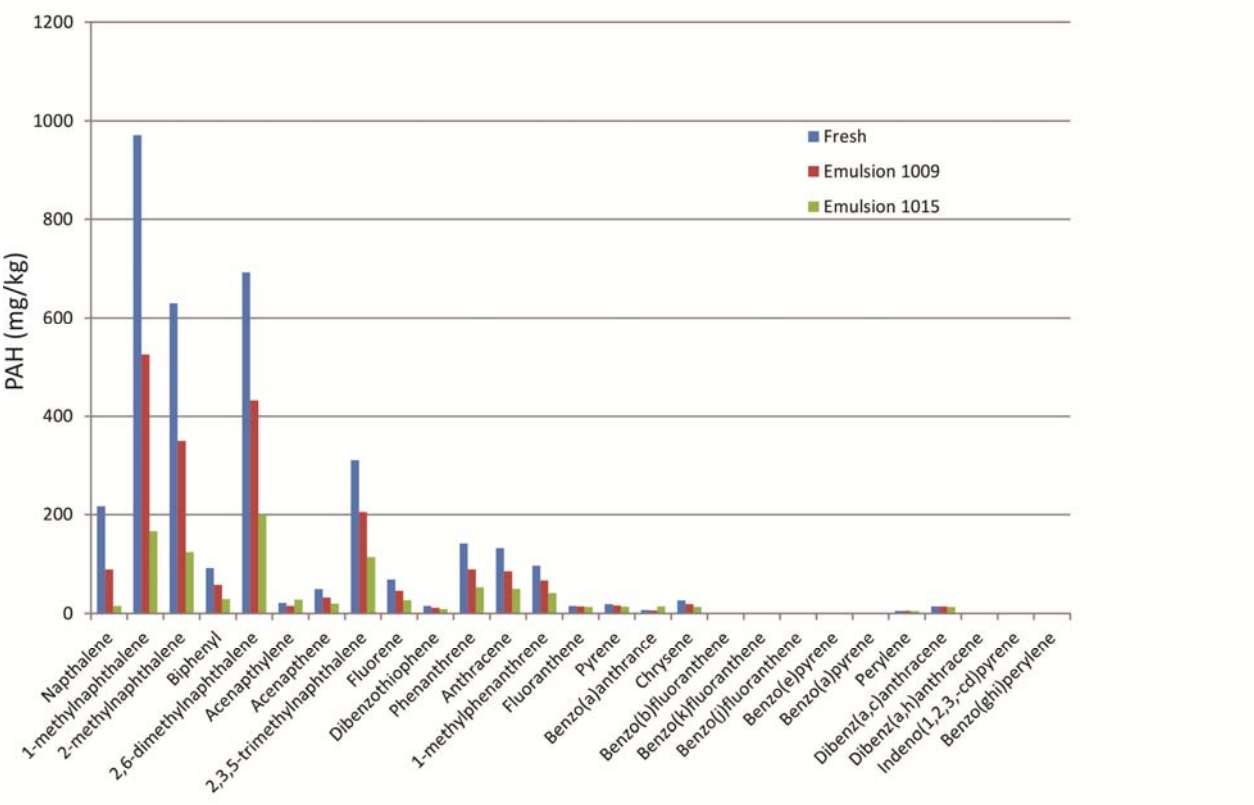

Figure 7. Change in PAH constituent chemistry for Texas intermediate crude oil during emulsion weathering experiment.

Figure 8 shows the change in individual PAH concentrations, normalized to a value of 1 for the unweathered oil on day 1. Results for acenaphtylene and benzo(a)anthracene on day 10 are considered anomolous. It is clear that the lower molecular weight PAHs (two- and three-ring compounds; towards the left side of the plot) were lost at a faster rate than higher molecular weight PAHs (towards the right side of the plot).

Figures 9-10 show the loss of total PAHs vs. time for the Texas intermediate oil under the three weathering conditions. Figure 11 shows the concentrating of individual PAHs in emulsion over time. Samples from weathering experiments in hood (evaporation and photo-oxidation) showed the slowest loss ($t_{1/2}$ = 108 days). Samples from uncontrolled weathering experiments outdoors weathered more quickly ($t_{1/2}$ = 44 days). Samples from emulsion weathering experiments weathered considerably faster ($t_{1/2}$ = 5 days), and are consistent with weathering observed during the Deepwater Horizon accident a (Hazen, 2010).

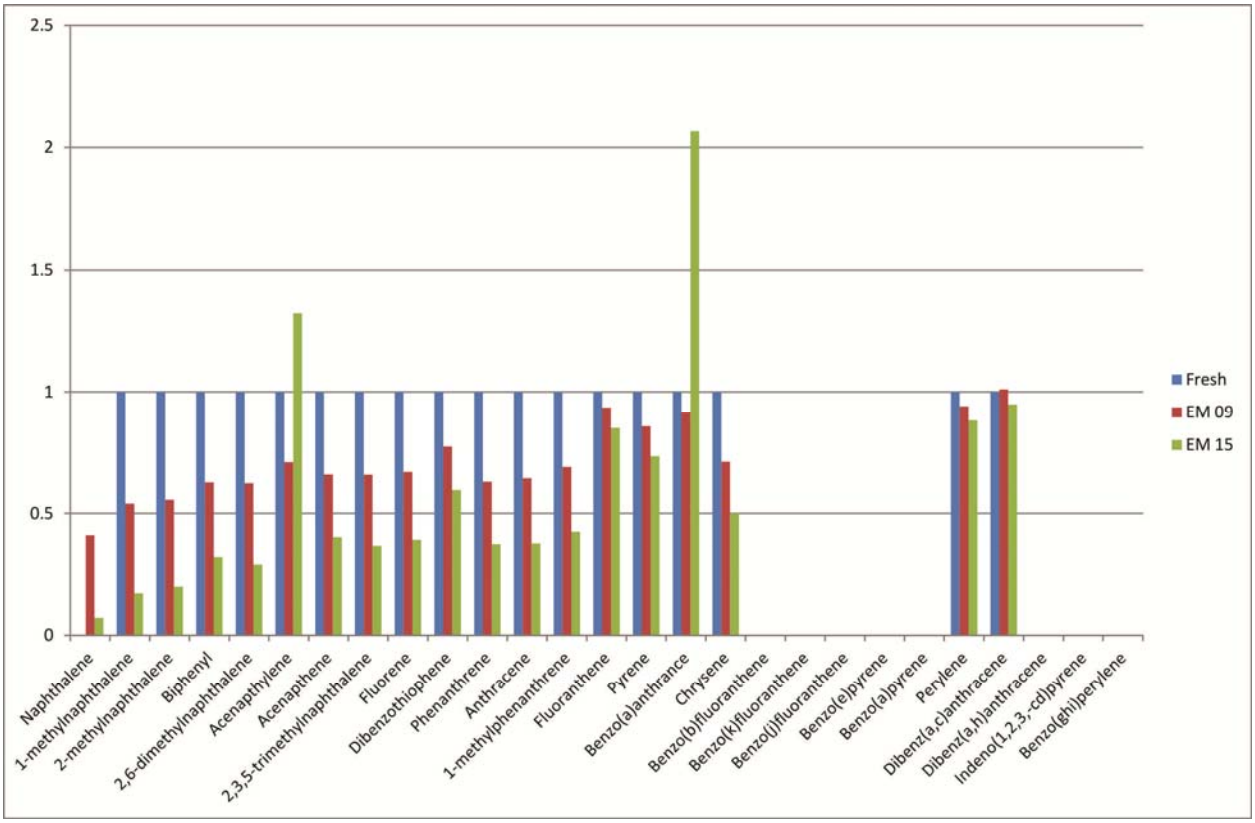

Figure 8. Results of Texas intermediate emulsion weathering, normalized by individual PAHs in un-weathered Texas intermediate raw crude oil.

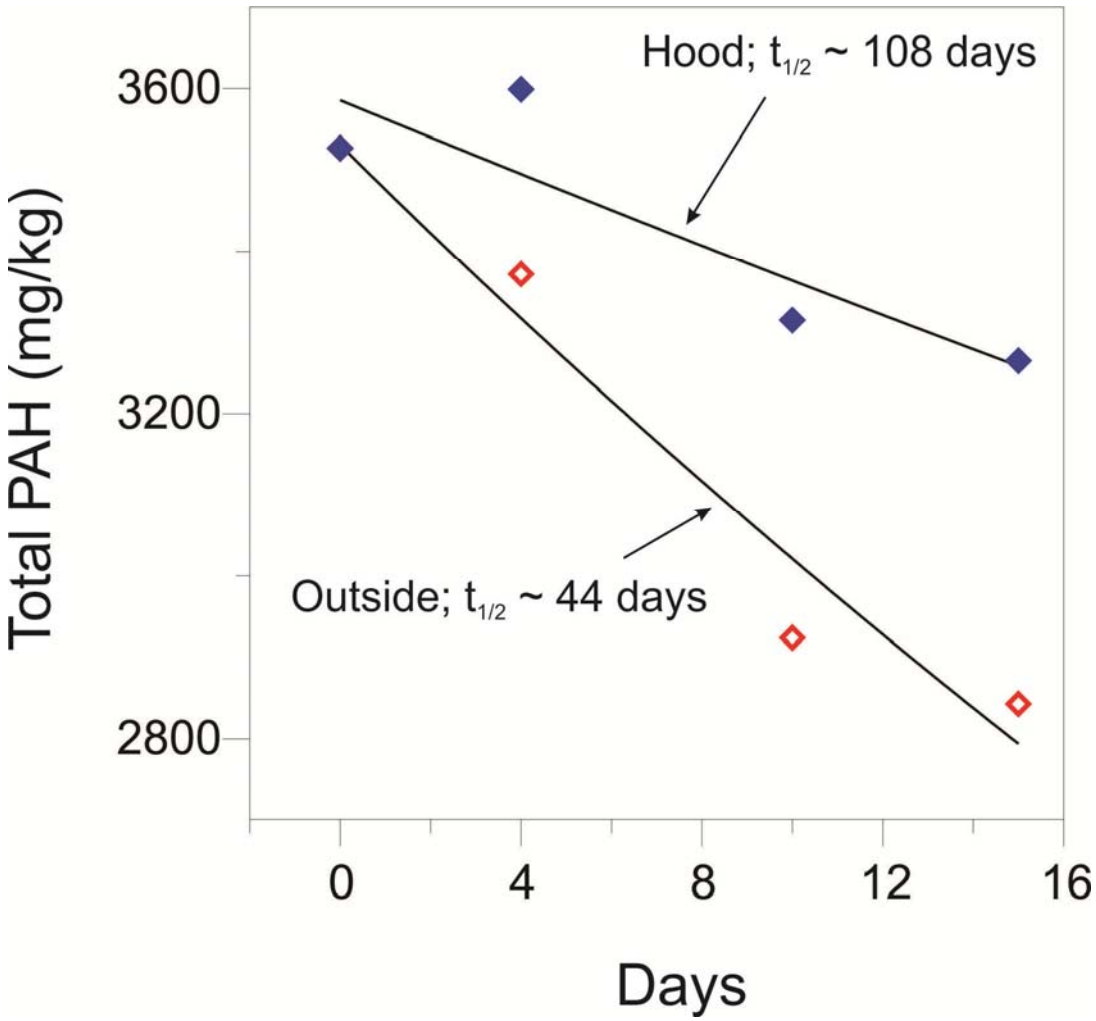

Figure 9. PAH degradation rates for Texas intermediate non-emulsion weathering experiments.

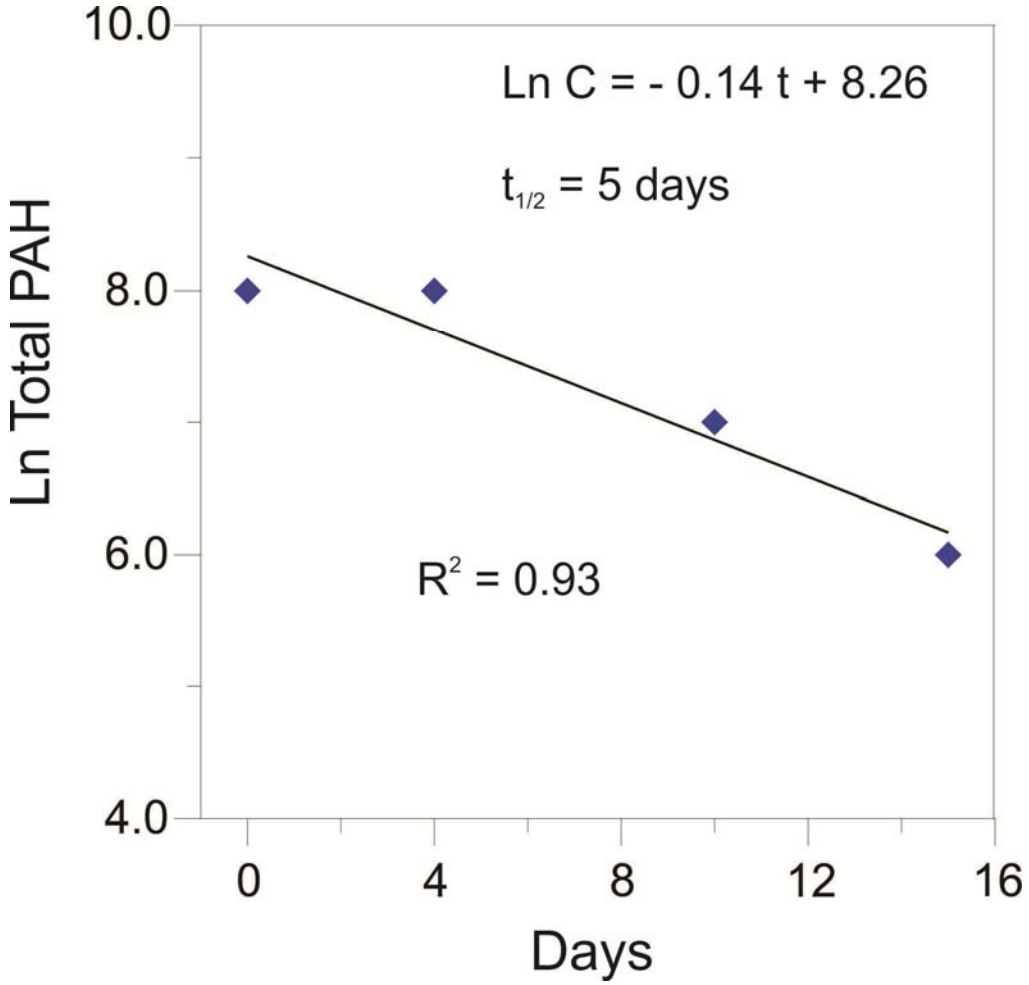

Figure 10. PAH degradation rate for Texas intermediate emulsion weathering experiment.

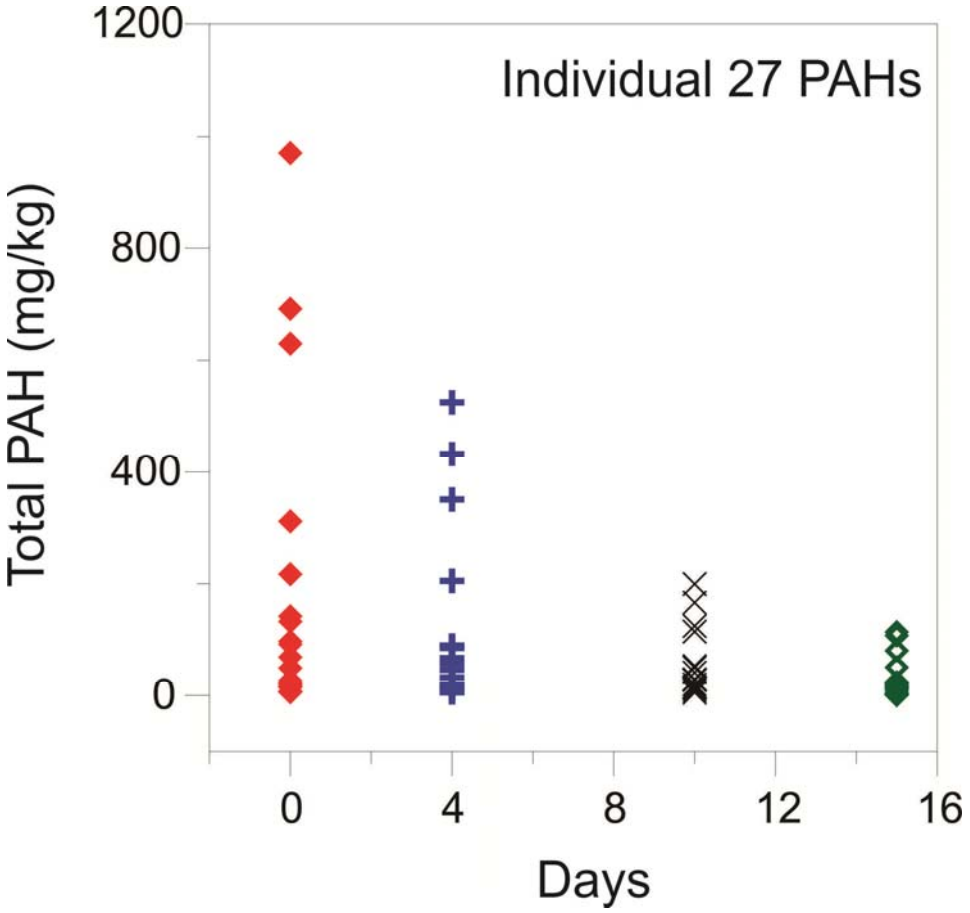

Figure 11. Mass loss and concentrating effect of individual PAHs in Texas intermediate emulsion weathering experiment.

Ancillary Information Necessary for Creation of Stable Emulsions and for the Performance of De-Emulsification Experiments

Determination of Asphaltene Content in Oils. W/O emulsions are stabilized by asphaltene molecules naturally present in the crude oil. Asphaltenes are large molecular weight compounds with variety of chemical species including short alkyl chains, 3-10 aromatic rings and hetero atoms like oxygen, nitrogen and sulfur and different functional groups including acids and bases (Djuve et al., 2001; Poteau et al., 2005). When an W/O emulsion is formed, asphaltene molecules present in the oil arrange themselves at the water-oil interface and increases the strength of the interfacial film, thus preventing the coalescence of water droplets (Djuve et al., 2001). As the age of the emulsion increases, more and more asphaltene molecules are driven to the water-oil interface from the bulk oil phase, strengthening the interfacial film and further increasing the stability of the emulsion (Poteau et al., 2005).

We examined several rapid semi-quantitative approaches to determine their effectiveness and applicability in our experiments. The semi-quantitative approaches we examined are discussed below.

1. Decantation Method. In this method, 1 g of oil is extracted into 30 mL of hexane. The solution is vortexed for 5 seconds and allowed to stand for 4 hours. The clear solution is decanted and the precipitate is dried in the oven at 70°C and weighed to determine the asphaltene content.

2. Filtration Method. In this method, 1 g of oil is extracted into 30 mL of hexane. The solution is vortexed for 5 seconds and filtered under vacuum through P42 filter paper. The filter paper is dried in oven at 70°C, weighed and the asphaltene content is determined.

3. Centrifuge Method. In this method, 1 g of oil is extracted into 30 mL of hexane in a 50 ml Oak Ridge centrifuge tube. The solution is vortexed for 5 seconds, and then centrifuged at 15000 rpm at 10°C for 60 minutes. The clear solution is then decanted and the precipitate in the tubes is dried in oven at 70°C and weighed to determine the asphaltene content.

The asphaltene fraction of the Texas intermediate oil, using the three semi-quantitative methods described above, is shown in Table 4. Of the three methods, the centrifuge method appears to provide the most consistent value and has the lowest standard deviation value.

Table 4. Asphaltene Fraction in Texas Intermediate Oil

Method	Asphaltene Fraction		
	%	Avg	SD
Decantation	5.82	8.193667	3.498207
	6.55		
	12.211		
Filtration	8.72	6.7655	2.76408
	4.811		
Centrifuge	4.49	4.445	0.06364
	4.4		

Artificial Sea Water With and Without Dispersant. Methods for creating standard Artificial Sea Water (ASW) with and without dispersant, at fixed pH were developed. The general approach was to dissolve sodium chloride in deionized water (3.3 % w/v), and adjust the solution pH using either sodium hydroxide solution or hydrochloric acid solution.

Preparation of Stable Emulsions

The general approach we employed for creating stable W/O emulsions involved the homogenization and mixing of raw crude oil with standard seawater, standard seawater plus dispersant, and standard seawater plus polar compound-modified dispersant. We investigated the feasibility of four potential methods for preparing emulsions (discussed below).

Rotary Mixer Method. The rotary mixer method has been used in the past to create stable W/O emulsions (e.g., Fingas and Fieldhouse, 2009). For our approach, 21 mL of pH-adjusted ASW was combined with 9 mL of oil (7:3 water:oil) in a glass container, placed on rotary mixer, and thermally equilibrated. Water and oil were mixed in the rotary mixer for 24 hours until a stable emulsion was formed.

Blender Method. The blender method has also been used in the past to create stable W/O emulsions (Fingas et al., 1996). For our approach, 70 mL of pH-adjusted ASW was combined with 30 mL of oil and thermally equilibrated. The W/O emulsion was prepared using a stainless steel laboratory-grade blender (Fingas et al., 1996). The mixture was then agitated in the blender at 30-second intervals until a stable emulsion was formed.

Sonicator Method. The sonicator method was developed by our research team as a possible alternative approach for creating stable W/O emulsions. In this method, 21 mL of pH-adjusted ASW was combined with 9 mL oil (7:3 water:oil) in a glass container, placed in a sonicator water bath, and thermally equilibrated. The sonicator frequency (4kHz) and time of sample exposure for emulsion formation (30 minutes) were determined by trial and error.

Homogenizer Method. A homogenizer method was examined by our research team as another possible alternative approach for creating stable W/O emulsions. In this method, 21 mL of pH-adjusted ASW was combined with 9 mL oil in a 50 mL Oak Ridge centrifuge tube (7:3 water:oil) and thermally equilibrated. The mixture was homogenized at 20000 rpm for 3 minutes.

Photomicrographs of W/O emulsions formed using the four methods noted above are shown in Figures 12 and 13. The photomicrographs shown in Figures 12-13 and others generated during this project indicate that the homogenizer method was more effective at creating stable W/O emulsions than are the rotary mixer, blender, and sonicator methods. The main disadvantage of blender method is that it requires large quantities of oil and ASW relative to the homogenizer method. Thus, the homogenizer method was used to create all standard emulsions used during the study.

A number of homogenizer emulsion experiments were performed to optimize this emulsion formation technique. Parameters varied included rotation speed, homogenization time, standing (equilibration) time, water-oil ratio, and pH of ASW. These experiments indicate that

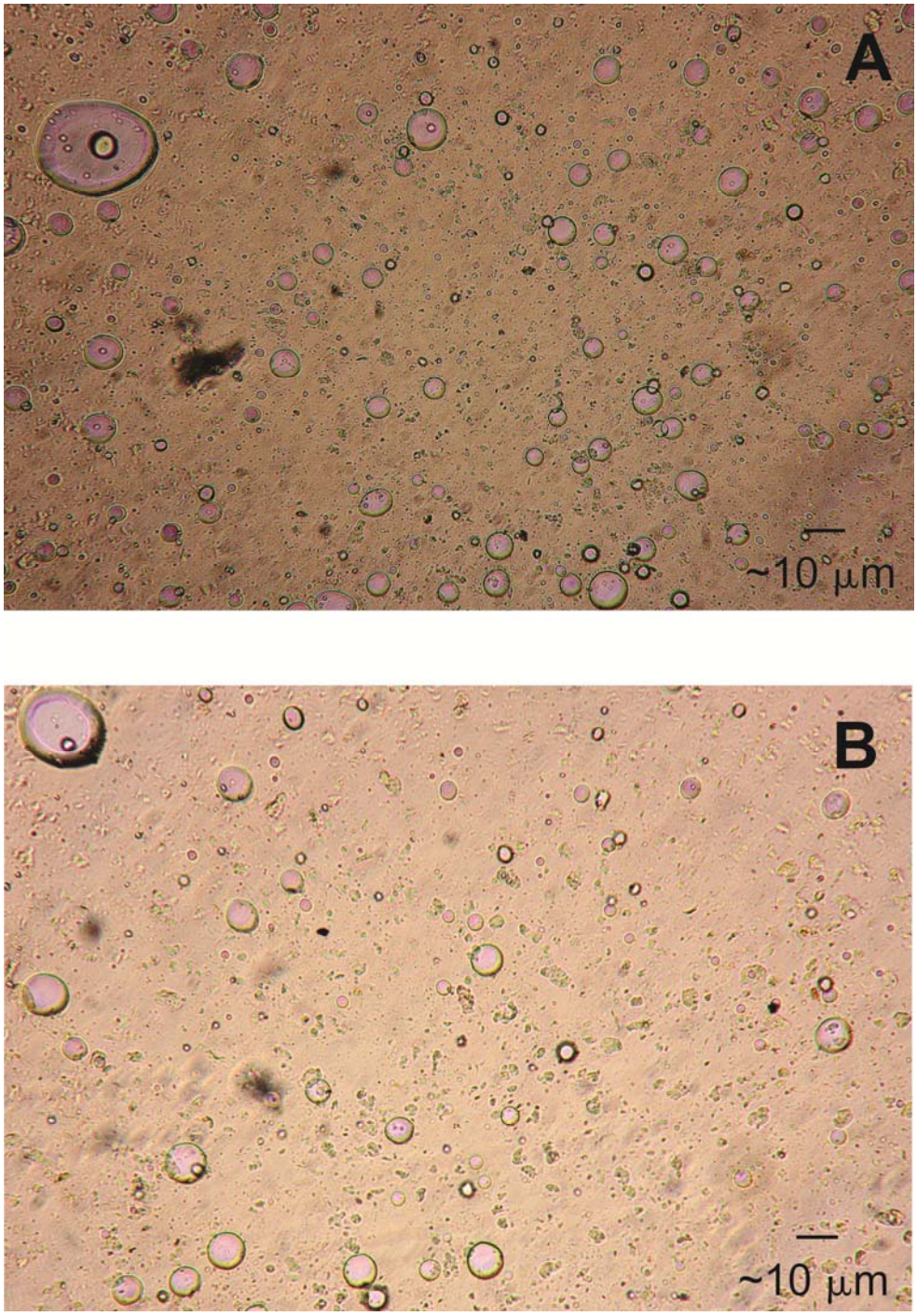

Figure 12. Photomicrographs of W/O emulsion created using (A) rotary mixer method, and (b) sonicator method.

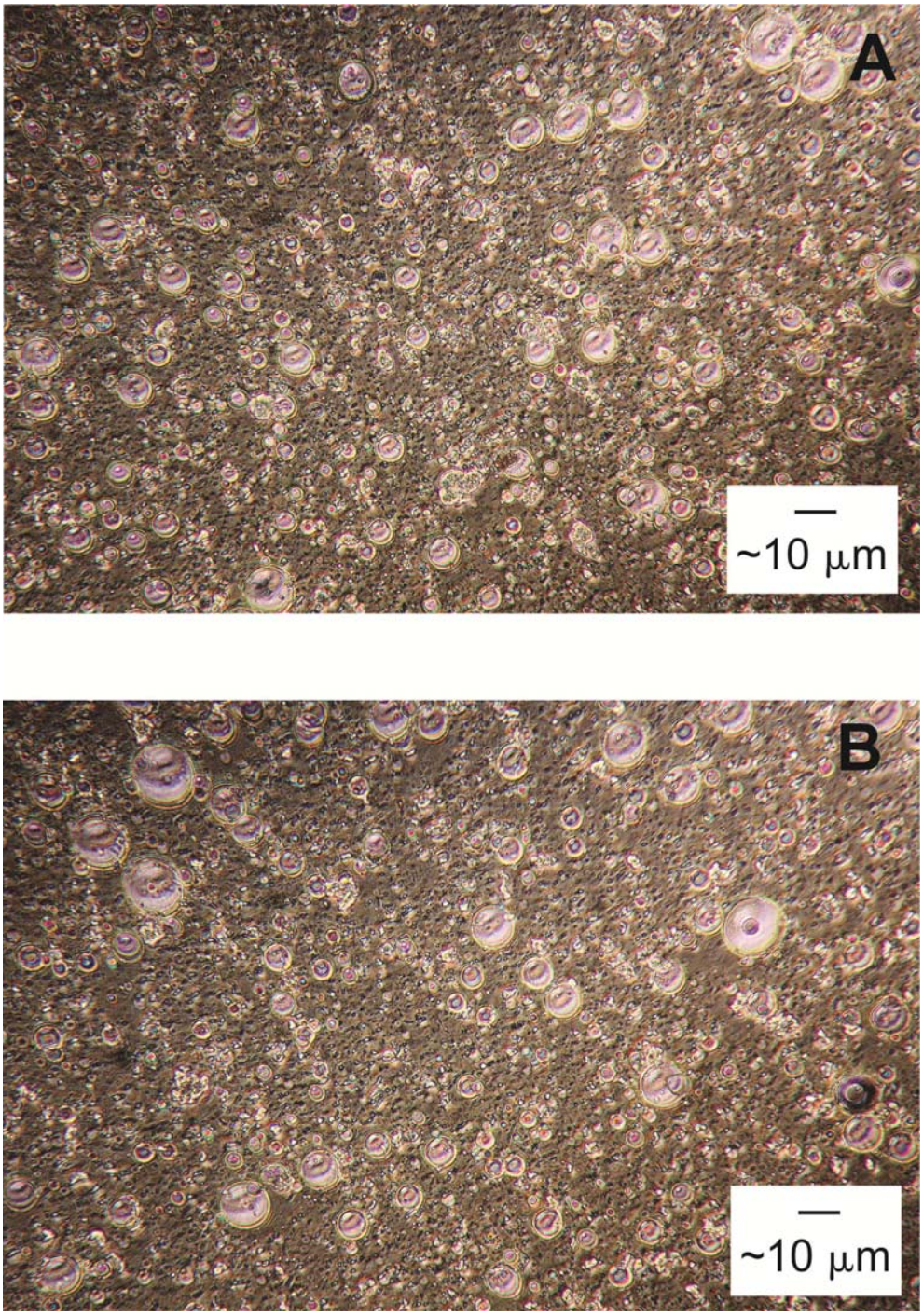

Figure 13. Photomicrographs of W/O emulsions created using (A) blender method, and (B) homogenizer method.

the optimum mixing speed and duration to form a stable W/O emulsion with minimum sized water droplets (<1-10µm) is 20000 rpm for 3 minutes.

Resolving Water from Stable Emulsions

Preliminary experiments were performed to optimize the experimental approach to be used to resolve water from de-stabilized emulsions. The general approach included (1) preparation of stable W/O emulsion using homogenizer method (discussed above); (2) transfer of stable emulsion to 50 mL Oak Ridge centrifuge tubes; (3) 24 hour equilibration; (4) centrifuged at 15000 rpm for approximately 60 minutes. The temperature of the centrifuge was maintained at 10°C. After centrifuging, the oil layer and emulsion were decanted, and the volume of resolved water was determined. The relative stability of the emulsion was considered inversely proportional to the quantity of water resolved.

We examined the stability of W/O emulsions created with varied-pH ASW exposed to the centrifugation approach. The stability of these emulsions should be relatively insensitive to the centrifugation method when de-stabilization approaches have not been used. The following parameters were considered: standing time, centrifuge speed and duration, ASW pH, and varied W:O ratio. The effect of these parameters on emulsion stability are discussed below.

Standing Time. The standing time between W/O emulsion preparation and centrifugation was varied and the % water resolved was determined. The centrifuge parameters were fixed at 15000 rpm for 60 minutes, with ASW pH of 12. There was no significant change in water resolved (Figure 14).

ASW pH. ASW pH was varied from 2 to 12 and its impact on % water resolved was determined. The centrifuge speed and time were 15000 rpm and 60 minutes, respectively, and the standing time was 24 hours. There was no significant change in effect on water resolved (Figure 16).

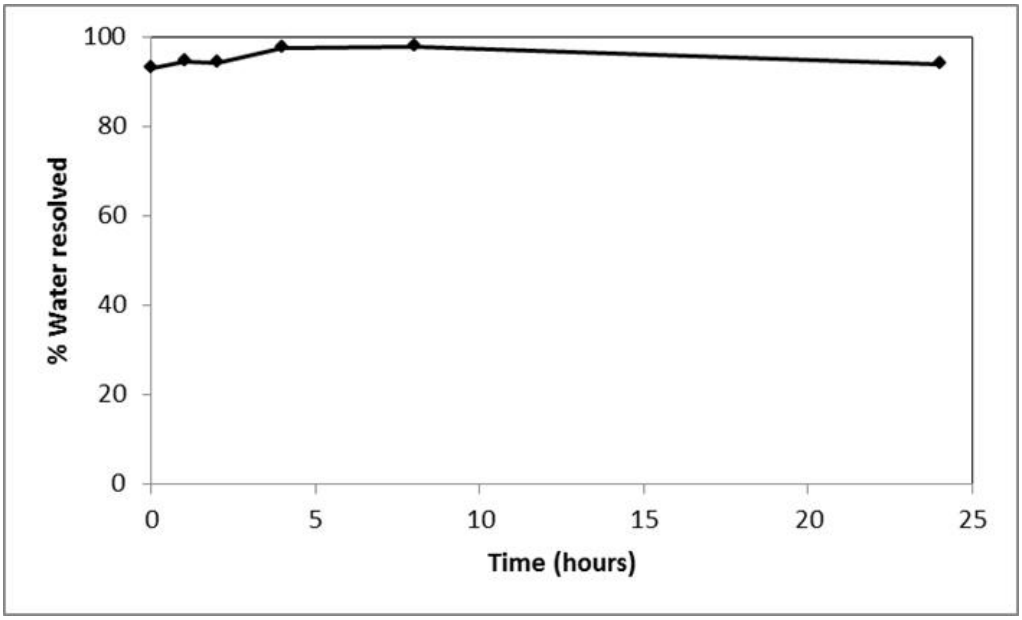

Figure 14. Percent water resolved from stable emulsion as a function of standing time.

Centrifuge Speed and Duration. The centrifuge speed and duration were varied from 10000 to 18500 rpm (maximum 20000 rpm), for 30 to 60 minutes respectively. ASW pH was 12, and standing time was 24 hours. There was no significant change in water resolved with respect to centrifuge parameters (Figure 15).

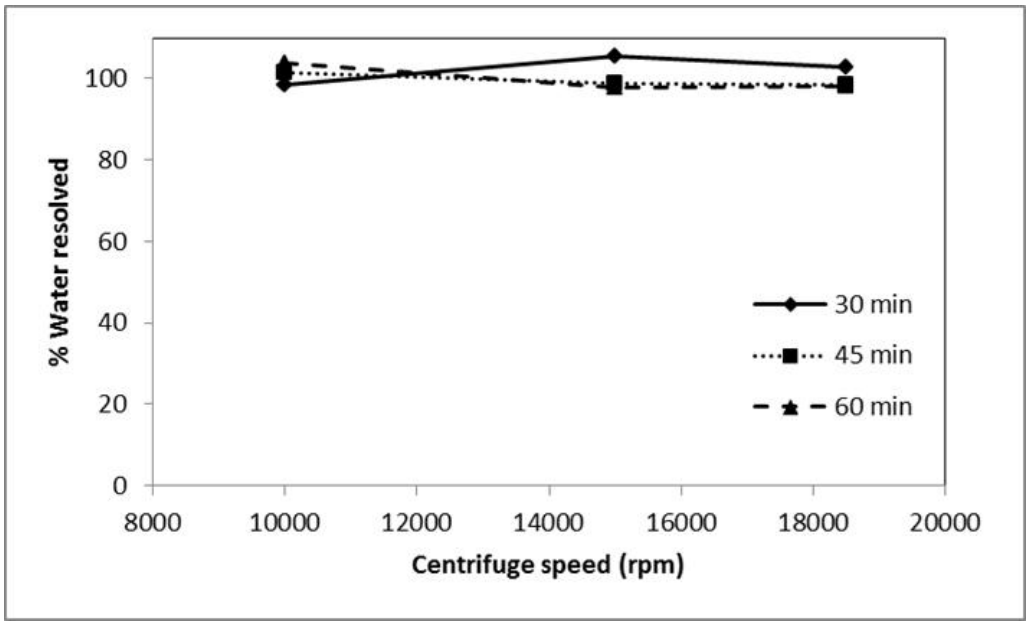

Figure 15. Percent water resolved from stable emulsion as a function of centrifuge speed and duration.

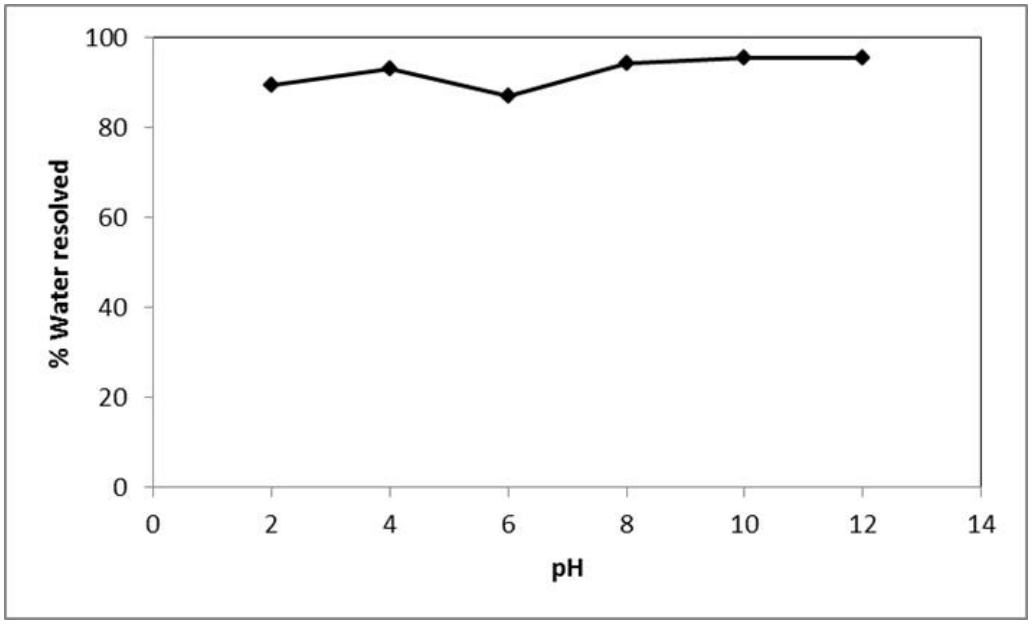

Figure 16. Percent water resolved from stable emulsion as a function of ASW pH.

Change in Water-Oil Ratio. The W:O ratio was varied as 7:3, 3:2 and 1:1. The centrifuge speed and time were 15000 rpm and 60 minutes, respectively, and the standing time was 24 hours. There was no significant effect on water resolved (Figure 17).

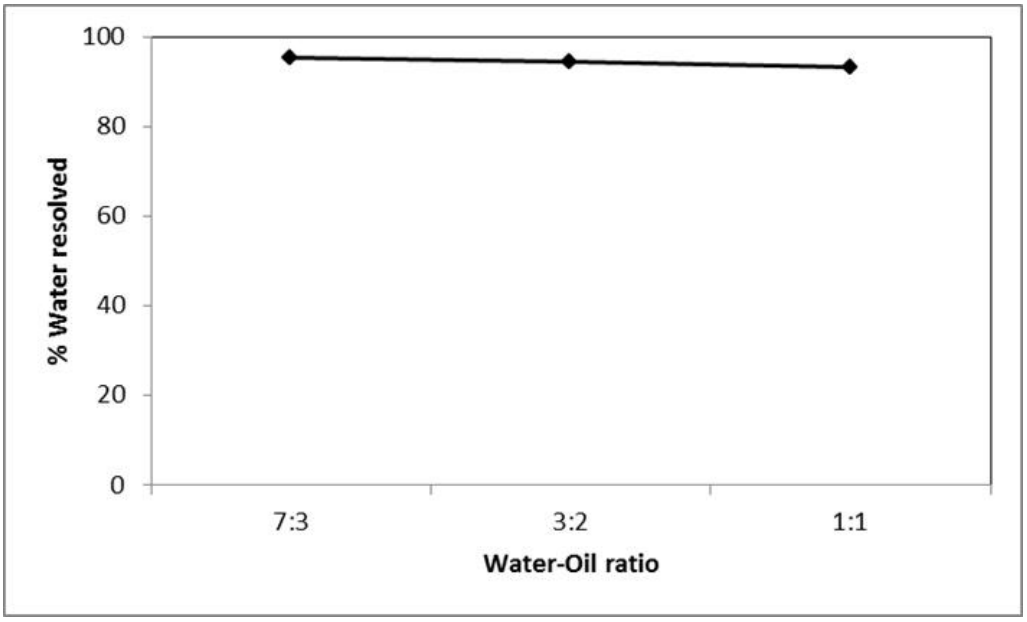

Figure 17. Percent water resolved from stable emulsion as a function of W:O ratio.

Part 2. Emulsion Destabilization Experiments

Characterization of Oil

Additional characterization of MC252 surrogate oil emulsions and actual MC252 emulsions were performed using the analytical approach described in Part 1. Characterization experiments for MC252 surrogate emulsions considered separate oil and emulsion phases generated as a result of homogenization and centrifugation of artificial emulsions (created using surrogate MC252 oil and simulated seawater). Homogenization and centrifugation of emulsions was a necessary step in examining the effectiveness of dispersants and modified dispersants in destabilizing emulsions. Our approach for creating artificial MC252 emulsions, and the process we followed for homogenization and centrifugation, are described in later sections of this report.

Results of the additional characterization experiments for MC252 surrogate oil emulsions are presented in Table 5 and Figures 18-19. These results show that for the surrogate MC252 emulsion without Corexit 9500, neither the clarified oil phase nor the clarified emulsion phase (phases separated following homogenization and centrifugation) are preferential phases for partitioning of the primary PAH compounds shown. For the surrogate MC252 emulsion with Corexit 9500 added (29:1 ratio of MC252 oil:Corexit 9500), partitioning of primary PAH compounds is slightly favored in the clarified oil/dispersant phase relative to the emulsion phase. This is consistent with the expectation that Corexit will increase the favorability of the clarified oil phase as a partitioning medium for oil-related hydrophobic compounds relative to the clarified emulsion phase.

Table 5. PAH Concentrations in Clarified Surrogate MC252 oil and Emulsion Phases

Analyte	MPS raw	SD	MPSO clarified	SD	MPSE clarified	SD	MPSDO clarified	SD	MPSDE clarified	SD
Napthalene	654.82	0.01	652.51	1.47	619.96	1.50	663.12	5.56	487.10	0.47
Acenapthylene	43.46	0.62	43.60	0.49	41.08	1.01	42.79	0.90	33.01	0.11
Acenapthene	76.96	20.08	36.02	1.03	45.70	21.76	51.73	24.41	39.87	14.18
Fluorene	148.30	0.91	147.30	0.33	141.24	1.39	150.08	1.99	115.79	1.94
Phenanthrene	203.45	0.26	202.07	0.14	189.04	3.77	199.78	2.40	157.87	2.54
Anthracene	219.45	0.89	219.20	1.71	211.40	1.08	222.46	0.21	179.91	1.29
Fluoranthene	10.46	0.70	10.32	0.42	11.83	0.61	10.74	0.14	8.73	1.30
Pyrene	4.16	0.23	4.06	0.10	3.81	0.05	4.09	0.05	2.81	0.11
Benzo(a)anthracene	16.62	0.24	17.03	0.24	16.23	0.62	18.42	0.35	13.64	0.31
Chrysene	63.42	0.84	64.19	0.30	61.57	0.22	65.34	1.14	50.59	1.98
Benzo(b)fluoranthrene	7.35	0.01	7.28	0.36	6.84	0.31	7.30	0.20	5.77	0.24
Benzo(a)pyrene	0.79	0.02	0.80	0.18	0.80	0.12	0.77	0.02	0.58	0.09
Dibenz(a,h)anthracene/ Indeno(1,2,3,-cd)pyrene	0.14	0.05	0.13	0.06	0.17	0.01	0.18	0.19	0.16	0.19
Benzo(ghi)perylene	0.99	0.01	1.18	0.11	1.08	0.08	1.12	0.10	0.57	0.12

Units: mg/kg oil phase

SD: Standard deviation of multiple analyes

MPS raw: Raw Macondo Prospect surrogate oil

MPSO clarified: Clarified Macodo Prospect surrogate oil extracted following homogenization and centrifugation

MPSE clarified: Calrified Macodo Prospect surrogate oil emulsion extracted following homogenization and centrifugation

MPSDO clarified: Clarified Macodo Prospect surrogate oil/Corexit 9500 extracted following homogenization and centrifugation

MPSDE clarified: Clarified Macodo Prospect surrogate oil/Corexit 9500 emulsion extracted following homogenization and centrifugation

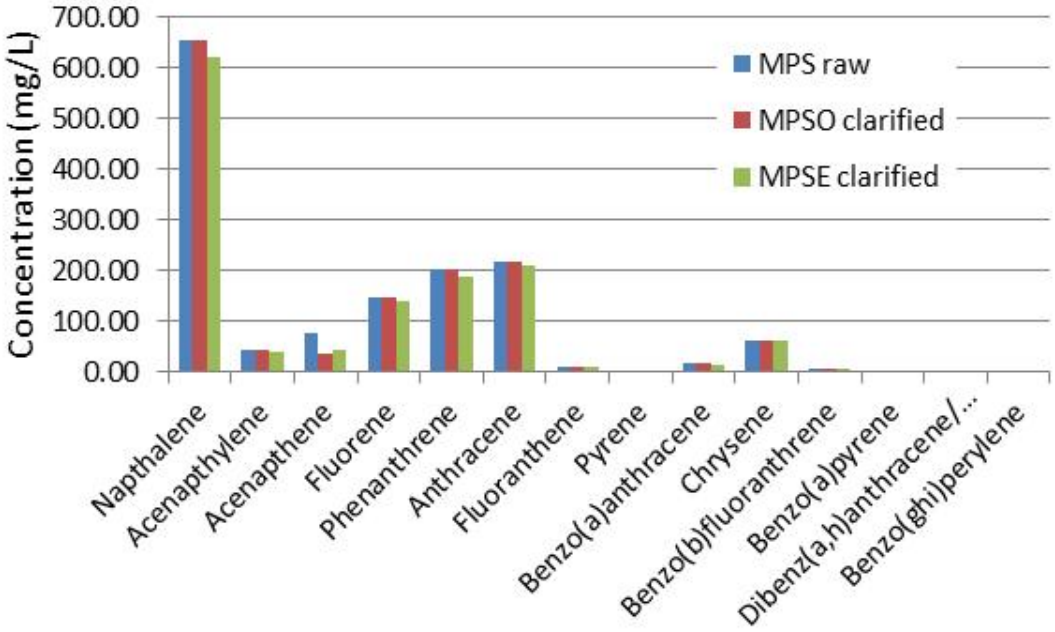

Figure 18. Concentration of PAHs in surrogate MC252 raw crude oil, surrogate MC252 clarified oil, and surrogate MC252 clarified emulsion phases (without Corexit 9500).

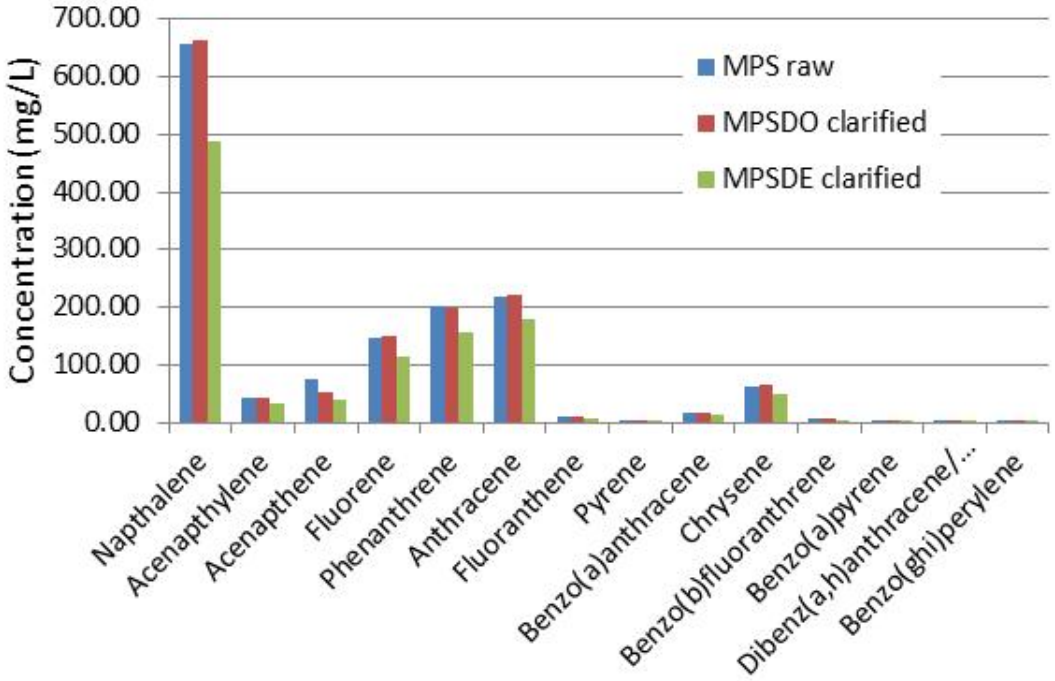

Figure 19. Concentration of PAHs in surrogate MC252 raw crude oil, surrogate MC252 clarified oil, and surrogate MC252 clarified emulsion phases (with Corexit 9500).

Actual MC252 emulsions were chemically characterized (considering the 16 EPA priority pollutant PAHs) using the analytical approach described above. Results are shown in Table 6 and Figure 20 compared to surrogate MC252 raw crude oil. These results show that for a number of target PAHs, a considerable amount of chemical weathering occurred between the time of emulsion formation and the time of collection on Alabama beaches in June 2010. Notable exceptions to this include chrysene, pyrene, benzo(b)fluoranthrene, benzo(a)pyrene, dibenz(a,h)anthracene/indeno(1,2,3,-cd)pyrene, and benzo(ghi)perylene. Several of these more recalcitrant compounds exhibit a concentrating effect (when concentration is determined on a per oil mass basis).

Table 6. PAH Concentration in Actual MC252 Emulsion Compared to Surrogate MC252 Raw Crude Oil

Analyte	MPS raw	SD	MPE	SD
Napthalene	654.82	0.01	1.9	0.1
Acenapthylene	43.46	0.62	1.14	0.03
Acenapthene	76.96	20.08	3.37	0.04
Fluorene	148.30	0.91	1.66	0.02
Phenanthrene	203.45	0.26	31	1
Anthracene	219.45	0.89	0	0
Fluoranthene	10.46	0.70	4.7	0.3
Pyrene	4.16	0.23	8.2	0.3
Benzo(a)anthracene	16.62	0.24	0.77	0.02
Chrysene	63.42	0.84	64	3
Benzo(b)fluoranthrene	7.35	0.01	7.7	0.3
Benzo(a)pyrene	0.79	0.02	3.63	0.02
Dibenz(a,h)anthracene/ Indeno(1,2,3,-cd)pyrene	0.14	0.05	1.39	0.02
Benzo(ghi)perylene	0.99	0.01	3.82	0.03

Units: mg/kg oil phase
SD: Standard deviation of multiple analyses
MPS raw: Raw Macondo Prospect surrogate oil
MPE: Actual Macondo Prospect emulsion

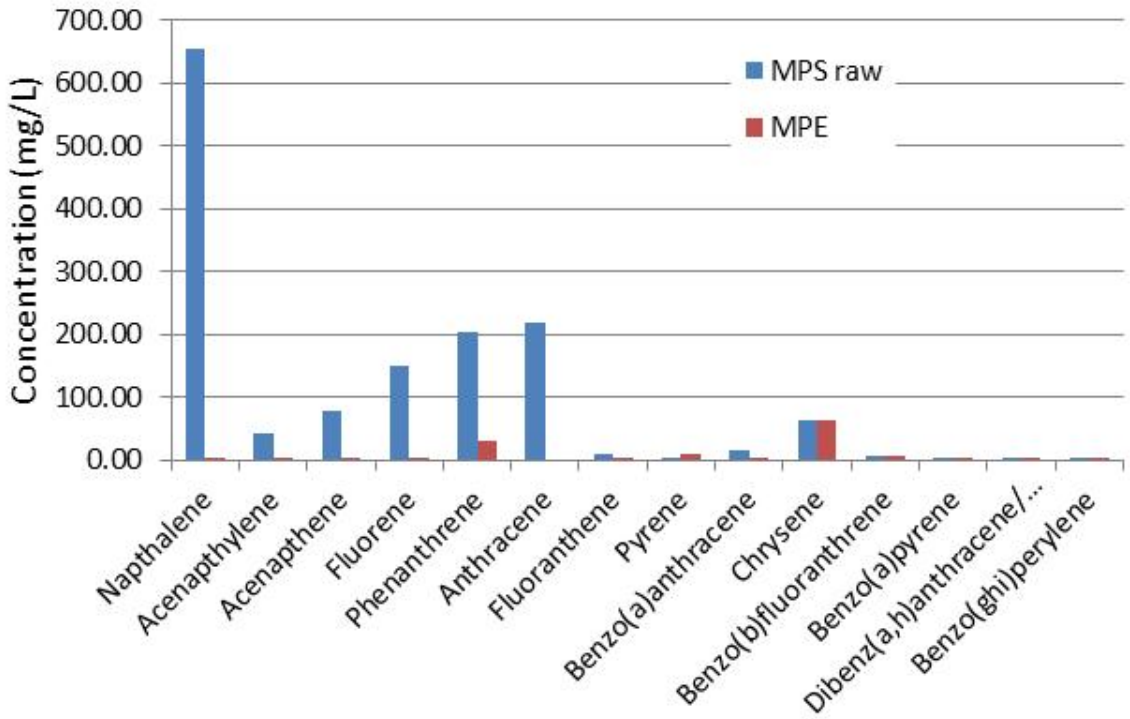

Figure 20. Concentration of PAHs in actual MC252 emulsion compared to surrogate MC252 raw crude oil.

Emulsion Destabilization Experiments

Part 1 of this report describes a number of experiments designed to determine the most effective methods for preparing stable emulsions using surrogate oil (both Texas Intermediate and surrogate MC252 oil), determine asphaltene content of emulsions, and to resolve and account for resolved water from stable and destabilized emulsions. The methods discussed here are based on these results.

Artificial Sea Water With and Without Corexit. Artificial Sea Water (ASW) with and without dispersant were prepared by dissolving sodium chloride in deionized water (3.3 % w/v), and adjusting the solution pH as needed using either sodium hydroxide solution or hydrochloric acid solution.

Artificial Emulsion Stability With and Without Corexit. The experiments performed to examine destabilizing W/O emulsions can be generally categorized as shown in Table 7. For the experiments considering emulsion stability as a function of ASW pH, two oil types were considered (Texas Intermediate and MC252 surrogate). For both oil types, artificial W/O emulsions without Corexit were prepared by adding 4 ml of pH adjusted ASW to 4 mL of oil (1:1 ASW:oil) and homogenizing at 20,000 rpm for 3 minutes. The emulsion was then transferred to a 10 mL centrifuge tube and allowed to stand for 12 hours. The contents were then centrifuged at 15,000 rpm for 60 minutes. After centrifugation, three distinct layers were formed: an upper layer comprised of clarified oil resolved from the W/O emulsion, an intermediate layer comprising the clarified, stable W/O emulsion, and a lower layer comprised of water resolved from the W/O emulsion (Figure 21). The clarified oil and clarified stable emulsion using MC252 surrogate oil at ASW pH 8 (average seawater) without Corexit were used to generate the chemical characterization results presented in Table 5.

For both types of oil, artificial W/O emulsions with Corexit were prepared similar to that described above, with the exception that Corexit was added to the oil phase (oil:Corexit 29:1) prior to the homogenization step. The clarified oil and clarified stable emulsion using MC252 surrogate oil at ASW pH 8 with Corexit were also used to generate the chemical characterization results presented in Table 5.

For both oil types with and without Corexit, the amount of water resolved following the centrifugation step was used to determine the effect of ASW pH on emulsion stability. Experimental conditions for emulsion stability verse pH using Texas Intermediate oil without Corexit are shown in Table 8. Similarly, experimental conditions for emulsion stability verses pH using Texas Intermediate oil with Corexit are shown in Table 9.

Results of the emulsion stability verses ASW pH with and without Corexit, using Texas Intermediate oil, are shown in Figure 22. This figure suggests that emulsion stability (as indicated by the amount of water resolved) for this oil is relatively insensitive to ASW pH within the range reasonably expected for seawater. At low and high ASW pH, the presence of Corexit appears to stabilize the emulsion (compared to no Corexit).

Table 7. General Emulsion Destabilizing Experiments

Experiment	Condition
Emulsion stability vs. pH	Texas Intermediate without Corexit
	Texas Intermediate with Corexit
	MC252 surrogate without Corexit
	MC252 surrogate with Corexit
Resolved emulsion stability vs. modified Corexit	MC252 surrogate
	Actual Mc252 emulsion

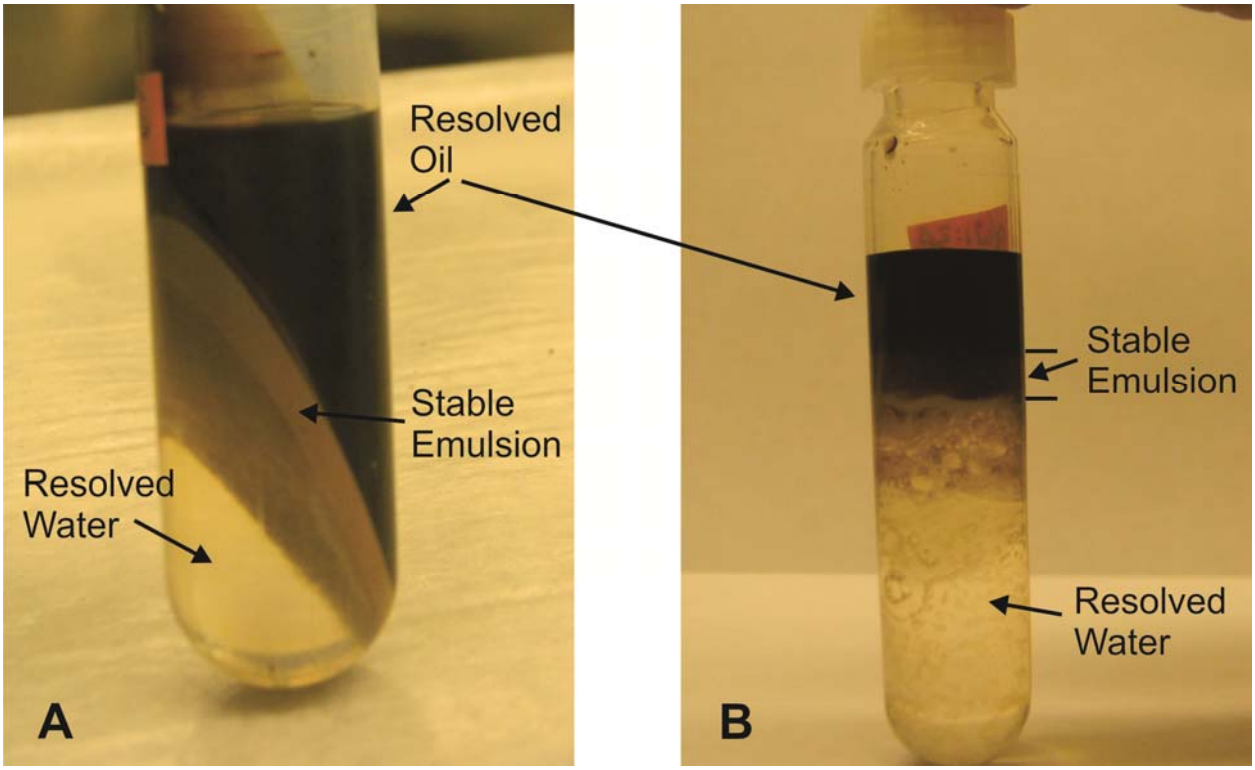

Figure 21. Resolved clarified oil, clarified stable emulsion, and resolved water following centrifugation step (MC252 surrogate oil; A: no Corexit; B: with Corexit).

Table 8. Conditions for Emulsion Stability vs. pH Experiments (Texas Intermediate; no Corexit)

Sample	Oil (mL)	ASW		Water resolved			
		pH	mL	mL	%	Avg	SD
pH2A	4	2	4	3.3	82.5	84.17	0.21
pH2B	4	2	4	3.2	80		
pH2C	4	2	4	3.6	90		
pH4A	4	4	4	3.4	85	86.67	0.12
pH4B	4	4	4	3.4	85		
pH4C	4	4	4	3.6	90		
pH6A	4	6	4	3.4	85	85.00	0.00
pH6B	4	6	4	3.4	85		
pH6C	4	6	4	3.4	85		
pH8A	4	8	4	3.4	85	88.33	0.12
pH8B	4	8	4	3.6	90		
pH8C	4	8	4	3.6	90		
pH10A	4	10	4	3.4	85	86.67	0.12
pH10B	4	10	4	3.4	85		
pH10C	4	10	4	3.6	90		
pH12A	4	12	4	3.2	80	83.33	0.12
pH12B	4	12	4	3.4	85		
pH12C	4	12	4	3.4	85		

Total sample volume: 8 mL

Artificial sea water (ASW): 3.3 5 w/v NaCl

Oil: Texas Intermediate

Oil/water ratio: 1:1

Homogenizer speed: 20,000 rpm

Homogenizing time: 3 minutes

Centrifuge speed: 15,000 rpm

Centrifuge time: 60 minutes

Table 9. Conditions for Emulsion Stability vs. pH Experiments (Texas Intermediate; with Corexit)

Sample	Oil (mL)	ASW		Water resolved			
		pH	mL	mL	%	Avg	SD
pH2A	4	2	4	2.6	65	71.67	0.64
pH2B	4	2	4	2.4	60		
pH2C	4	2	4	3.6	90		
pH4A	4	4	4	3.4	85	83.33	0.12
pH4B	4	4	4	3.2	80		
pH4C	4	4	4	3.4	85		
pH6A	4	6	4	3.4	85	88.33	0.12
pH6B	4	6	4	3.6	90		
pH6C	4	6	4	3.6	90		
pH8A	4	8	4	3.6	90	87.50	0.10
pH8B	4	8	4	3.4	85		
pH8C	4	8	4	3.5	87.5		
pH10A	4	10	4	3.2	80	80.00	0.20
pH10B	4	10	4	3	75		
pH10C	4	10	4	3.4	85		
pH12A	4	12	4	3	75	78.33	0.23
pH12B	4	12	4	3.4	85		
pH12C	4	12	4	3	75		

Total sample volume: 8 mL

Artificial sea water (ASW): 3.3 5 w/v NaCl

Oil: Texas Intermediate

Oil/water ratio: 1:1

Dispersant: Corexit 9500

Oil/Dispersant ratio: 29:1

Homogenizer speed: 20,000 rpm

Homogenizing time: 3 minutes

Centrifuge speed: 15,000 rpm

Centrifuge time: 60 minutes

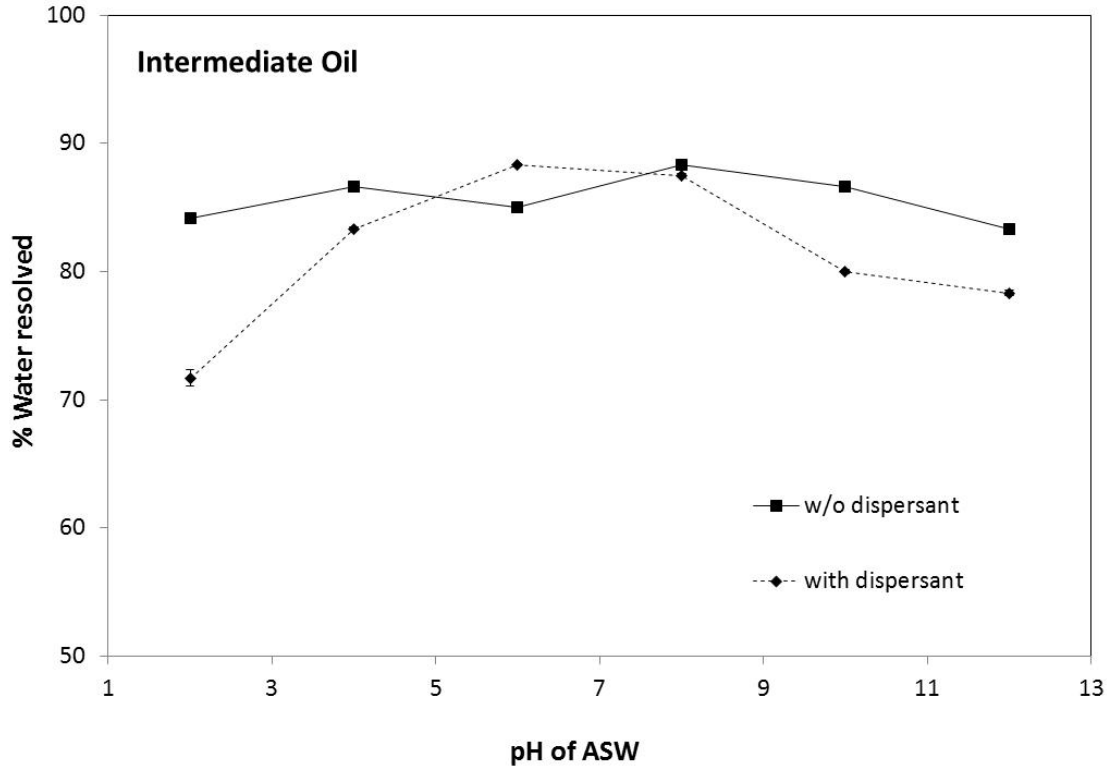

Figure 22. Water resolved from Texas Intermediate emulsion (with and without Corexit) as a function of ASW pH.

Experimental conditions for emulsion stability verse pH using MC252 surrogate oil without Corexit are shown in Table 10. Similarly, experimental conditions for emulsion stability verses pH using MC252 surrogate oil with Corexit are shown in Table 11.

Results of the emulsion stability verses ASW pH with and without Corexit, using MC252 surrogate oil, are shown in Figure 23. This figure suggests that emulsion stability (as indicated by the amount of water resolved) for this oil is relatively insensitive to ASW pH when Corexit is present. When Corexit is not present, the emulsion appears relatively stable at low pH, but becomes unstable at pH greater than 9.

Based on the results of the ASW pH-dependent emulsion stability experiments, we elected to conduct all remaining experiments using an ASW pH of 8 (approximating normal seawater).

Table 10. Conditions for Emulsion Stability vs. pH Experiments (MC252 surrogate; no Corexit)

Sample	Oil (mL)	ASW		Water resolved			
		pH	mL	mL	%	Avg	SD
pH2A	4	2	4	3.4	85	85.00	0.00
pH2B	4	2	4	3.4	85		
pH2C	4	2	4	3.4	85		
pH4A	4	4	4	2.8	70	80.00	0.35
pH4B	4	4	4	3.4	85		
pH4C	4	4	4	3.4	85		
pH6A	4	6	4	3.2	80	78.33	0.12
pH6B	4	6	4	3	75		
pH6C	4	6	4	3.2	80		
pH8A	4	8	4	3.4	85	86.67	0.12
pH8B	4	8	4	3.4	85		
pH8C	4	8	4	3.6	90		
pH10A	4	10	4	3.2	80	76.67	0.12
pH10B	4	10	4	3	75		
pH10C	4	10	4	3	75		
pH12A	4	12	4	0.4	10	9.17	0.06
pH12B	4	12	4	0.4	10		
pH12C	4	12	4	0.3	7.5		

Total sample volume: 8 mL

Artificial sea water (ASW): 3.3 5 w/v NaCl

Oil: MC252 surrogate

Oil/water ratio: 1:1

Homogenizer speed: 20,000 rmp

Homogenizing time: 3 minutes

Centrifuge speed: 15,000 rmp

Centrifuge time: 60 minutes

Table 11. Conditions for Emulsion Stability vs. pH Experiments (MC252 surrogate; with Corexit)

Sample	Oil (mL)	ASW		Water resolved			
		pH	mL	mL	%	Avg	SD
pH2A	4	2	4	3.6	90	90.00	0.00
pH2B	4	2	4	3.6	90		
pH2C	4	2	4	3.6	90		
pH4A	4	4	4	3.6	90	91.67	0.12
pH4B	4	4	4	3.6	90		
pH4C	4	4	4	3.8	95		
pH6A	4	6	4	3.2	80	88.33	0.31
pH6B	4	6	4	3.8	95		
pH6C	4	6	4	3.6	90		
pH8A	4	8	4	3.4	85	90.00	0.20
pH8B	4	8	4	3.6	90		
pH8C	4	8	4	3.8	95		
pH10A	4	10	4	3.8	95	93.33	0.12
pH10B	4	10	4	3.8	95		
pH10C	4	10	4	3.6	90		
pH12A	4	12	4	3.8	95	96.67	0.12
pH12B	4	12	4	4	100		
pH12C	4	12	4	3.8	95		

Total sample volume: 8 mL

Artificial sea water (ASW): 3.3 5 w/v NaCl

Oil: MC252 surrogate

Oil/water ratio: 1:1

Dispersant: Corexit 9500

Oil/Dispersant ratio: 29:1

Homogenizer speed: 20,000 rpm

Homogenizing time: 3 minutes

Centrifuge speed: 15,000 rpm

Centrifuge time: 60 minutes

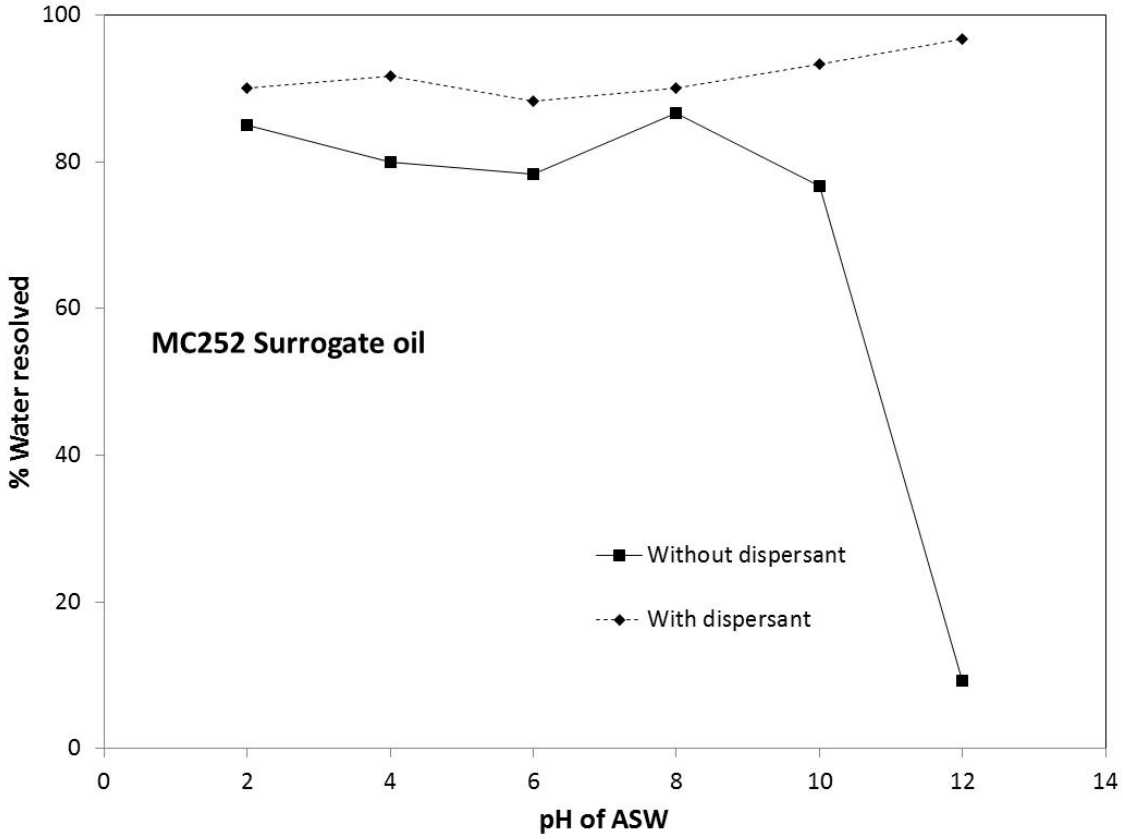

Figure 23. Water resolved from MC252 surrogate emulsion (with and without Corexit) as a function of ASW pH.

Destabilizing Artificial MC252 Surrogate Emulsions and Actual MC252 Emulsions Using Modified Corexit.

Experiments were performed to examine the effect of two polar additives to Corexit 9500 on the stability of MC252 surrogate emulsions and actual MC252 emulsions. Both emulsions (MC252 surrogate and actual MC252) were prepared as previously described (for neat emulsion/ASW, emulsion with Corexit, and emulsion with modified Corexit).

Selection of Polar Additives to Modify Corexit

Two polar additives were selected for modifying Corexit 9500: octanol and hexylamine. These compounds were selected based on their mechanistic differences in destabilizing emulsions and their low aquatic toxicity (Martin and Young, 2001). Octanol is a short-chain alcohol, which acts to break down existing intermolecular hydrogen bonds between asphaltene molecules, replacing them with alcohol-asphaltene hydrogen bonds (Sjöblom et al., 2003). Wasan et al. (1979) observed a similar destabilization effect on W/O emulsions originating from a medium-chain alcohols. Wasan et al. (1979) studied the influence of co-surfactants, such as n-hexanol, on crude oil-aqueous surfactant systems. They found that the co-surfactant increased the rate of emulsion destabilization and attributed the observed higher water coalescence rates to a reduction in interfacial rigidity. Hexylamine acts to disintegrate asphaltenes through interaction between the nitrogen group (base) and the acid groups present in the interfacial film. A consequence of this interaction is that the properties of the interfacial film are modified, with this film becoming hydrophilic to stabilize the aqueous droplets (Sjöblom et al., 1990; Sjöblom et al., 2003.

Experiments Using MC252 Surrogate Emulsions

Results of experiments considering stability of MC252 surrogate emulsions treated with Corexit and octanol-modified Corexit are shown in Table 12 and Figure 24. Results of experiments considering stability of MC252 surrogate emulsions treated with Corexit and hexylamine-modified Corexit are shown in Table 13 and Figure 25. These results indicate that both octanol and hexylamine do not appreciably increase the destabilizing effects of Corexit in MC252

surrogate emulsions. Stated another way, these results suggest that neat Corexit is as effective in destabilizing emulsions formed using MC252 surrogate oil as Corexit modified with the selected polar compounds. This is possibly a result of the abundance of non-asphaltene compounds within the surrogate emulsion, which would tend to reduce the interfacial properties within the emulsion and allow water to coalesce more effectively under centrifugation.

Table 12. Experimental Results for MC252 Surrogate Emulsions Treated with Corexit and Octanol-Modified Corexit

Sample	Trial No	Dispersant Ingredients (% Volume)			Dispersant/ Modified Dispersant: Oil Ratio	ASW Added (mL)	Emulsion Added (mL)	ASW Resolved		Water Resolved from Emulsion (mL)		
		Corexit	1 - Octanol	Hexylamine				mL	%	mL	avg	% ASW
Surrogate MC252 Emulsion	1	0	0	0	N/A	4	4	5.4	135	1.4	1.53	38.33
	2	0	0	0	N/A	4	4	5.6	140	1.6		
	3	0	0	0	N/A	4	4	5.6	140	1.6		
Emulsion + Corexit	1	100	0	0	1:29	4	4	6.8	170	2.8	2.87	71.67
	2	100	0	0	1:29	4	4	6.8	170	2.8		
	3	100	0	0	1:29	4	4	7	175	3		
C+O 10%	1	90	10	0	1:29	4	4	6.8	170	2.8	2.87	71.67
	2	90	10	0	1:29	4	4	7	175	3		
	3	90	10	0	1:29	4	4	6.8	170	2.8		
C+O 20%	1	80	20	0	1:29	4	4	6.6	165	2.6	2.67	66.67
	2	80	20	0	1:29	4	4	6.6	165	2.6		
	3	80	20	0	1:29	4	4	6.8	170	2.8		
C+O 30%	1	70	30	0	1:29	4	4	6.6	165	2.6	2.60	65.00
	2	70	30	0	1:29	4	4	6.6	165	2.6		
	3	70	30	0	1:29	4	4	6.6	165	2.6		
C+O 40%	1	60	40	0	1:29	4	4	6.6	165	2.6	2.60	65.00
	2	60	40	0	1:29	4	4	6.6	165	2.6		
	3	60	40	0	1:29	4	4	6.6	165	2.6		
C+O 50%	1	50	50	0	1:29	4	4	6.8	170	2.8	2.73	68.33
	2	50	50	0	1:29	4	4	6.6	165	2.6		
	3	50	50	0	1:29	4	4	6.8	170	2.8		
Octanol 100%	1	0	100	0	1:29	4	4	6.2	155	2.2	2.13	53.33
	2	0	100	0	1:29	4	4	6	150	2		
	3	0	100	0	1:29	4	4	6.2	155	2.2		

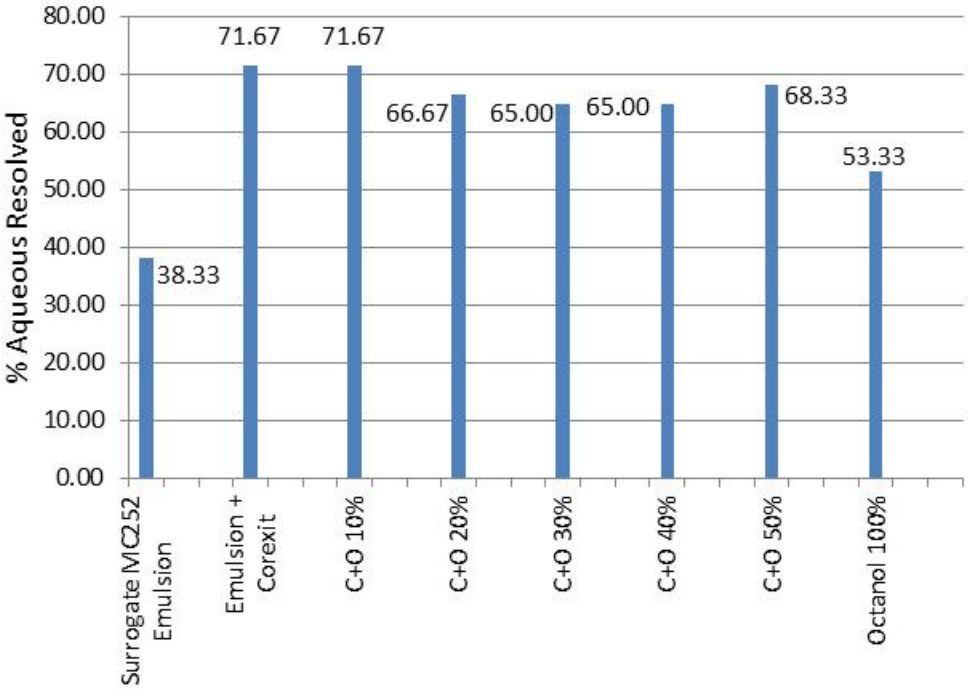

Figure 24. Average percent water resolved above ASW volume for MC252 surrogate emulsion (neat, treated with Corexit, treated with octanol-modified Corexit).

Table 13. Experimental Results for MC252 Surrogate Emulsions Treated with Corexit and Hexylamine-Modified Corexit

Sample	Trial No	Dispersant Ingredients (% Volume)			Dispersant/ Modified Dispersant: Oil Ratio	ASW Added (mL)	Emulsion Added (mL)	ASW Resolved		Water Resolved from Emulsion (mL)		
		Corexit	1 - Octanol	Hexylamine				mL	%	mL	avg	% ASW
Surrogate MC252 Emulsion	1	0	0	0	N/A	4	4	5.4	135	1.4	1.53	38.33
	2	0	0	0	N/A	4	4	5.6	140	1.6		
	3	0	0	0	N/A	4	4	5.6	140	1.6		
Emulsion + Corexit	1	100	0	0	1:29	4	4	6.8	170	2.8	2.87	71.67
	2	100	0	0	1:29	4	4	6.8	170	2.8		
	3	100	0	0	1:29	4	4	7	175	3		
C+H 10%	1	90	10	0	1:29	4	4	6.6	165	2.6	2.73	68.33
	2	90	10	0	1:29	4	4	6.8	170	2.8		
	3	90	10	0	1:29	4	4	6.8	170	2.8		
C+H 20%	1	80	20	0	1:29	4	4	6.8	170	2.8	2.87	71.67
	2	80	20	0	1:29	4	4	7	175	3		
	3	80	20	0	1:29	4	4	6.8	170	2.8		
C+H 30%	1	70	30	0	1:29	4	4	7	175	3	2.93	73.33
	2	70	30	0	1:29	4	4	6.8	170	2.8		
	3	70	30	0	1:29	4	4	7	175	3		
C+H 40%	1	60	40	0	1:29	4	4	6.8	170	2.8	2.80	70.00
	2	60	40	0	1:29	4	4	6.8	170	2.8		
	3	60	40	0	1:29	4	4	6.8	170	2.8		
C+H 50%	1	50	50	0	1:29	4	4	7	175	3	3.07	76.67
	2	50	50	0	1:29	4	4	7.2	180	3.2		
	3	50	50	0	1:29	4	4	7	175	3		
Hexylamine 100%	1	0	100	0	1:29	4	4	7	175	3	3.07	76.67
	2	0	100	0	1:29	4	4	7.2	180	3.2		
	3	0	100	0	1:29	4	4	7	175	3		

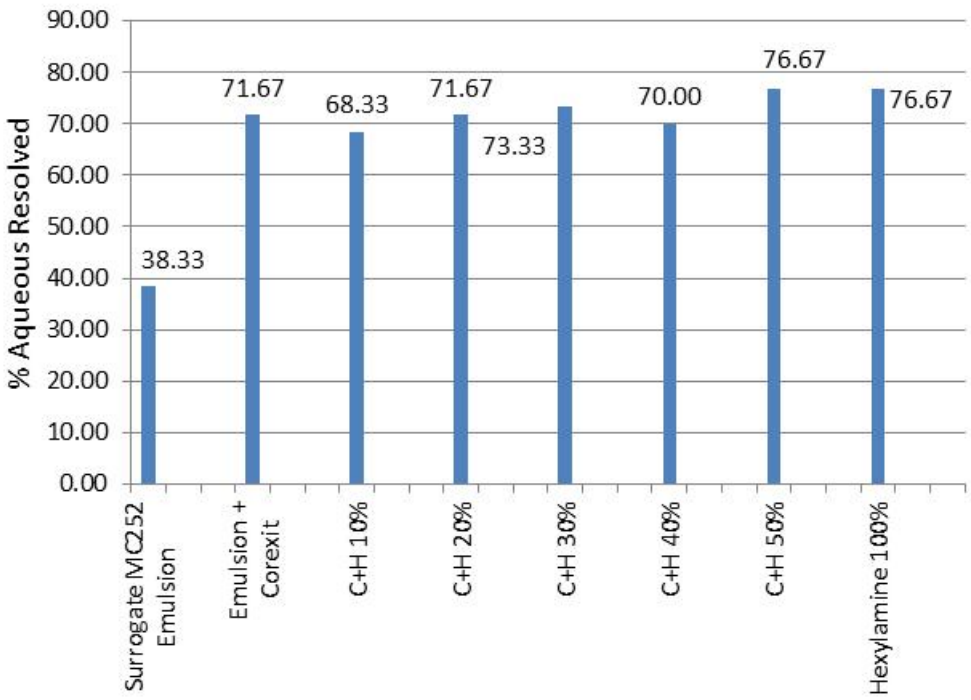

Figure 25. Average percent water resolved above ASW volume for MC252 surrogate emulsion (neat, treated with Corexit, and treated with hexylamine-modified Corexit).

Experiments Using Actual MC252 Emulsions

The actual MC252 emulsion collected along Alabama's beaches in June 2010 are highly viscous, and contain foreign particles (predominantly sand). This required a pre-treatment step prior to their use in these experiments. As pre-treatment, actual MC252 emulsion samples were placed in a sonicator bath at 40°C for 60 minutes to reduce viscosity and allow the majority of foreign particles to settle and be removed.

Results of experiments considering stability of actual MC252 emulsions treated with Corexit and octanol-modified Corexit are shown in Table 14 and Figures 26. Results of experiments considering stability of actual MC252 emulsions treated with Corexit and hexylamine-modified Corexit are shown in Table 15 and Figure 27. These results indicate that at volume fractions less than approximately 50%, both octanol and hexylamine do not appreciably increase the destabilizing effects of Corexit in actual MC252 emulsions. At volume fractions greater than 50%, these results indicate that both Corexit additives tend to increase the inclusion of water within the emulsion.

Our observations of the physical properties of the actual MC252 emulsion as the volume fraction of both Corexit additives increases indicate that the emulsion becomes less viscous, even though the amount of water resolved from the emulsion under centrifugation is considerably reduced. An indication of the reason for this apparent stability can be found when viewing photomicrographs of the clarified actual MC252 emulsion and the aqueous solution resolved from this emulsion under centrifugation. Figure 28 shows the clarified actual MC252 emulsion and the aqueous solution resolved from this emulsion under centrifugation (no Corexit or modified Corexit present). Figure 29 shows the same emulsion and water fractions following addition of 100% volume fraction of Corexit. These images demonstrate the effects of the presence of Corexit: aqueous droplets within the emulsion phase are smaller and more evenly distributed within the Corexit-treated emulsion relative to the neat emulsion. Additionally, more oil is present in the aqueous solution resolved from the Corexit-treated

Table 14. Experimental Results for Actual MC252 Emulsions Treated with Corexit and Octanol-Modified Corexit

Sample	Trial No	Dispersant Ingredients (% Volume)			Dispersant/ Modified Dispersant: Oil Ratio	ASW Added (mL)	Emulsion Added (mL)	ASW Resolved		Water Resolved from Emulsion (mL)		
		Corexit	1 - Octanol	Hexylamine				mL	%	mL	avg	% ASW
Actual MC252 Emuslion	1	0	0	0	N/A	4	4	3.6	90	-0.4	-0.33	-8.33
	2	0	0	0	N/A	4	4	3.6	90	-0.4		
	3	0	0	0	N/A	4	4	3.8	95	-0.2		
Emulsion + Corexit	1	100	0	0	1:29	4	4	4.6	115	0.6	0.53	13.33
	2	100	0	0	1:29	4	4	4.4	110	0.4		
	3	100	0	0	1:29	4	4	4.6	115	0.6		
C+O 10%	1	90	10	0	1:29	4	4	4.4	110	0.4	0.53	13.33
	2	90	10	0	1:29	4	4	4.6	115	0.6		
	3	90	10	0	1:29	4	4	4.6	115	0.6		
C+O 20%	1	80	20	0	1:29	4	4	4.4	110	0.4	0.53	13.33
	2	80	20	0	1:29	4	4	4.6	115	0.6		
	3	80	20	0	1:29	4	4	4.6	115	0.6		
C+O 30%	1	70	30	0	1:29	4	4	4.4	110	0.4	0.47	11.67
	2	70	30	0	1:29	4	4	4.6	115	0.6		
	3	70	30	0	1:29	4	4	4.4	110	0.4		
C+O 40%	1	60	40	0	1:29	4	4	4.2	105	0.2	0.40	10.00
	2	60	40	0	1:29	4	4	4.4	110	0.4		
	3	60	40	0	1:29	4	4	4.6	115	0.6		
C+O 50%	1	50	50	0	1:29	4	4	4.2	105	0.2	0.00	0.00
	2	50	50	0	1:29	4	4	4	100	0		
	3	50	50	0	1:29	4	4	3.8	95	-0.2		
Octanol 100%	1	0	100	0	1:29	4	4	3.6	90	-0.4	-0.20	-5.00
	2	0	100	0	1:29	4	4	4	100	0		
	3	0	100	0	1:29	4	4	3.8	95	-0.2		

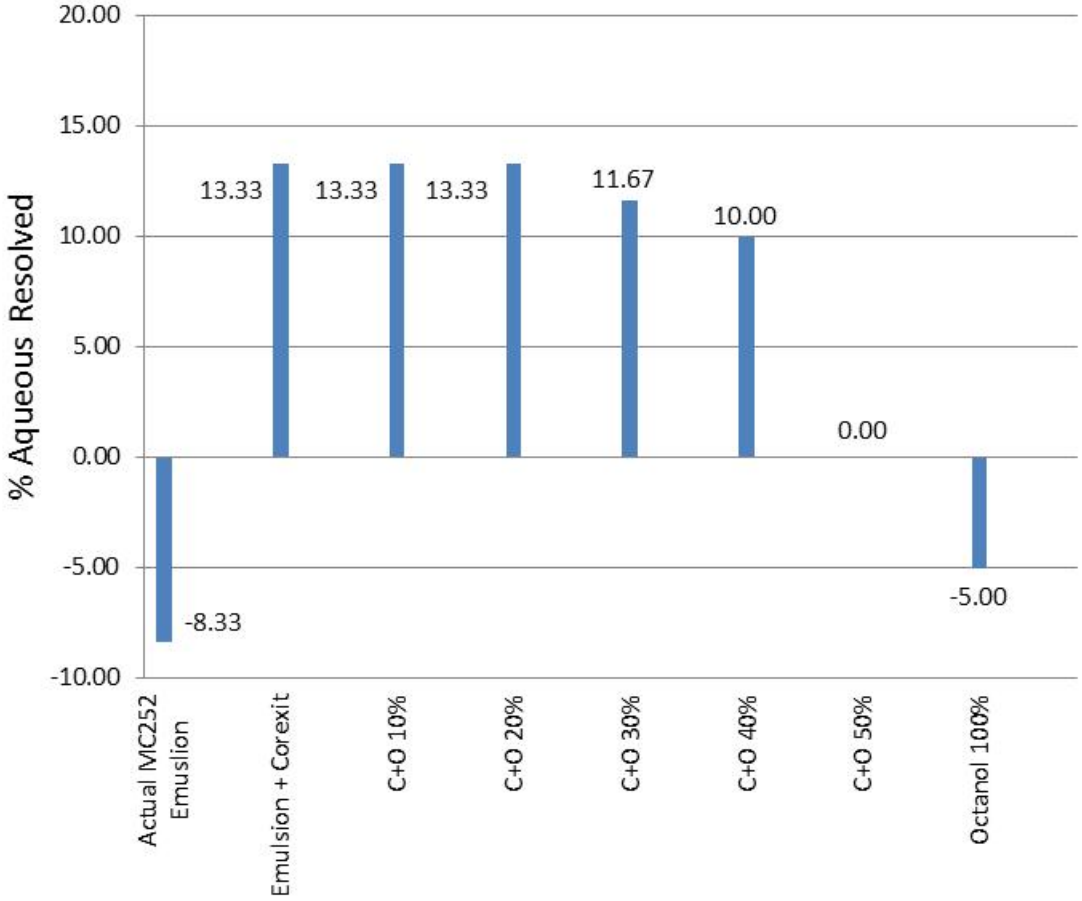

Figure 26. Average percent water resolved above ASW volume for actual MC252 emulsion (neat, treated with Corexit, treated with octanol-modified Corexit).

Table 15. Experimental Results for Actual MC252 Emulsions Treated with Corexit and Hexylamine-Modified Corexit

Sample	Trial No	Dispersant Ingredients (% Volume)			Dispersant/ Modified Dispersant: Oil Ratio	ASW Added (mL)	Emulsion Added (mL)	ASW Resolved		Water Resolved from Emulsion (mL)		
		Corexit	1 - Octanol	Hexylamine				mL	%	mL	avg	% ASW
Actual MC252 Emuslion	1	0	0	0	N/A	4	4	3.6	90	-0.4	-0.33	-8.33
	2	0	0	0	N/A	4	4	3.6	90	-0.4		
	3	0	0	0	N/A	4	4	3.8	95	-0.2		
Emulsion + Corexit	1	100	0	0	1:29	4	4	4.6	115	0.6	0.53	13.33
	2	100	0	0	1:29	4	4	4.4	110	0.4		
	3	100	0	0	1:29	4	4	4.6	115	0.6		
C+H 10%	1	90	10	0	1:29	4	4	4.4	110	0.4	0.40	10.00
	2	90	10	0	1:29	4	4	4.4	110	0.4		
	3	90	10	0	1:29	4	4	4.4	110	0.4		
C+H 20%	1	80	20	5	1:29	4	4	4.2	105	0.2	0.27	6.67
	2	80	20	5	1:29	4	4	4.2	105	0.2		
	3	80	20	5	1:29	4	4	4.4	110	0.4		
C+H 30%	1	70	30	10	1:29	4	4	4.4	110	0.4	0.40	10.00
	2	70	30	10	1:29	4	4	4.4	110	0.4		
	3	70	30	10	1:29	4	4	4.4	110	0.4		
C+H 40%	1	60	40	15	1:29	4	4	4.6	115	0.6	0.47	11.67
	2	60	40	15	1:29	4	4	4.2	105	0.2		
	3	60	40	15	1:29	4	4	4.6	115	0.6		
C+H 50%	1	50	50	5	1:29	4	4	4.4	110	0.4	0.27	6.67
	2	50	50	5	1:29	4	4	4.2	105	0.2		
	3	50	50	5	1:29	4	4	4.2	105	0.2		
Hexylamine 100%	1	0	100	15	1:29	4	4	4	100	0	-0.13	-3.33
	2	0	100	15	1:29	4	4	3.8	95	-0.2		
	3	0	100	15	1:29	4	4	3.8	95	-0.2		

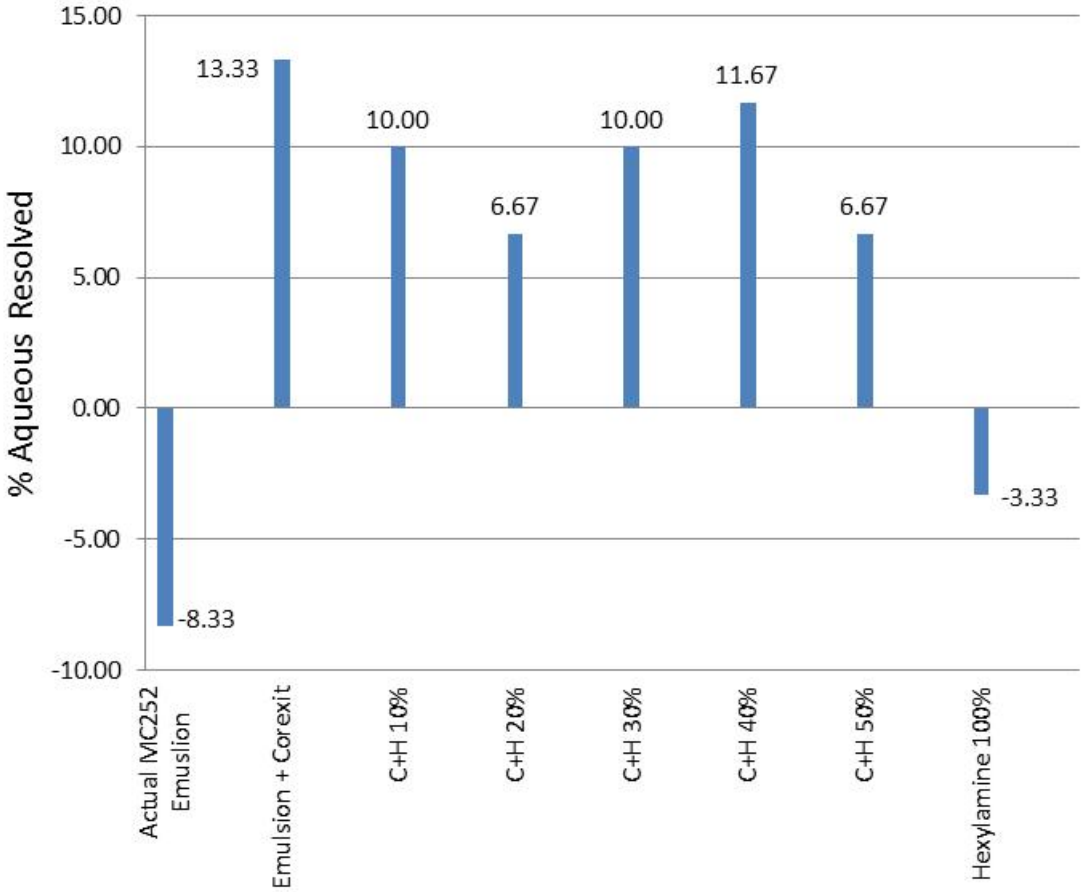

Figure 27. Average percent water resolved above ASW volume for actual MC252 emulsion (neat, treated with Corexit, treated with hexylamine-modified Corexit).

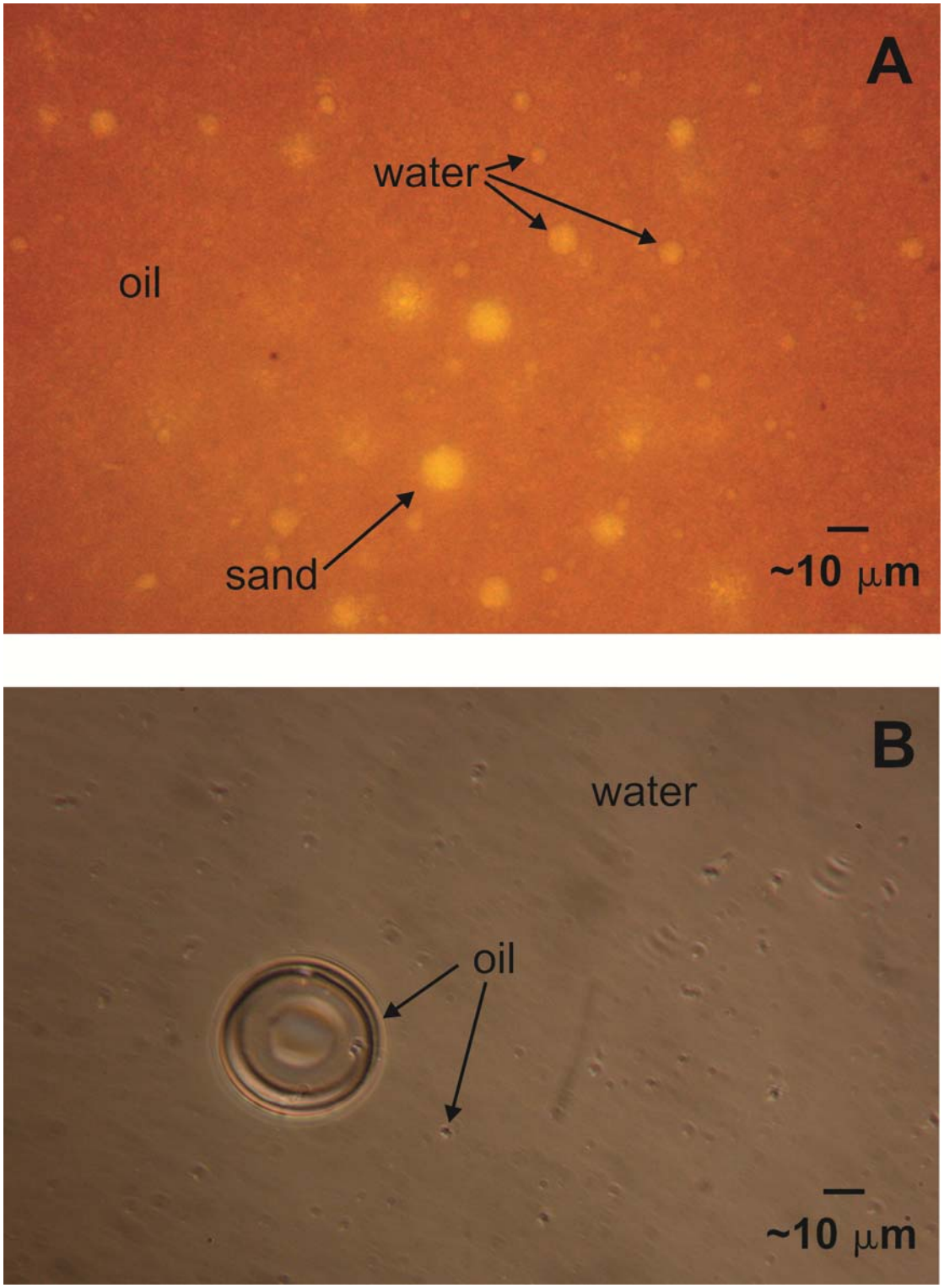

Figure 28. Clarified actual MC252 emulsion (A) and the aqueous solution resolved from this emulsion (B) under centrifugation (no Corexit or modified Corexit present).

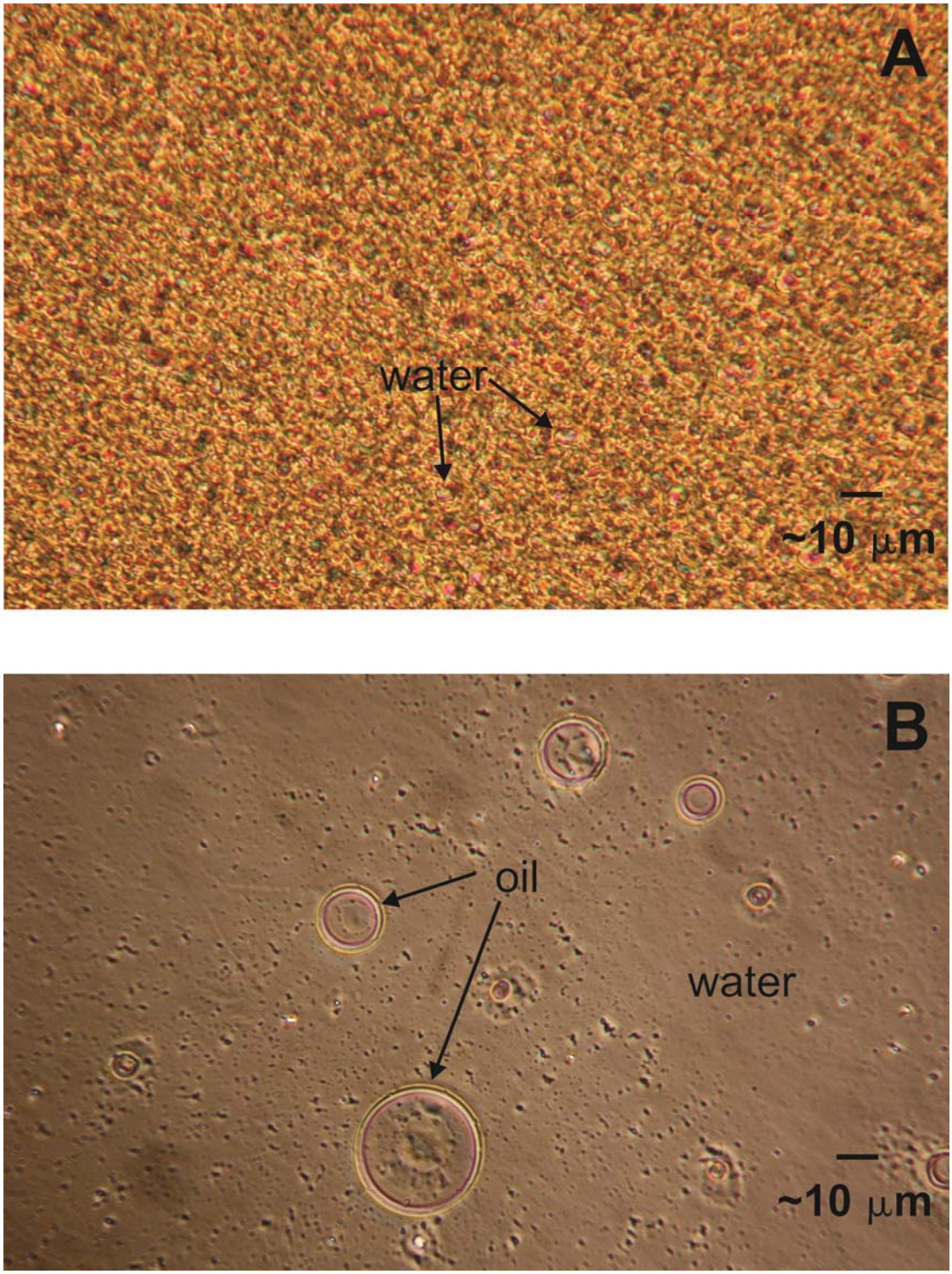

Figure 29. Clarified actual MC252 emulsion (A) and the aqueous solution resolved from this emulsion (B) under centrifugation (100% volume fraction Corexit).

emulsion than in the aqueous solution resolved from the neat emulsion. This physical behavior is a consequence of both the reduced interfacial tension between oil and aqueous solution within the emulsion (allowing for enhanced coalescence and removal of aqueous solution from the emulsion during centrifugation), and the increase in apparent aqueous solubility of oil.

Figure 30 shows the same emulsion and water fractions following addition of 50% volume Corexit and 50% volume octanol. Similar photomicrographs using 50% volume hexylamine were obtained. Under these conditions, the aqueous solution droplets within the emulsion are much smaller than those in the neat emulsion and in the emulsion where only Corexit was added. Further, oil appears as a more distinct separate phase in the resolved aqueous solution compared to the Corexit-only condition (Figure 29). Note from Figures 26 and 27 that at octanol or hexylamine volume fractions greater than approximately 50%, the amount of aqueous solution resolved from the emulsion decreases (and a fraction of added ASW is actually retained in the emulsion as the octanol or hexylamine volume fraction increases). With these considerations, Figure 30 suggests that the presence of octanol and hexylamine above approximately 50% volume results in the formation of a microemulsion, which although accommodating more water, is destabilized with respect to viscosity (significantly reduced) and the increased presence of separate phase oil in the aqueous phase. This transition to a microemulsion is beneficial because of the enhanced ability for physicochemical weathering and biological degradation to take place relative to stable W/O emulsions.

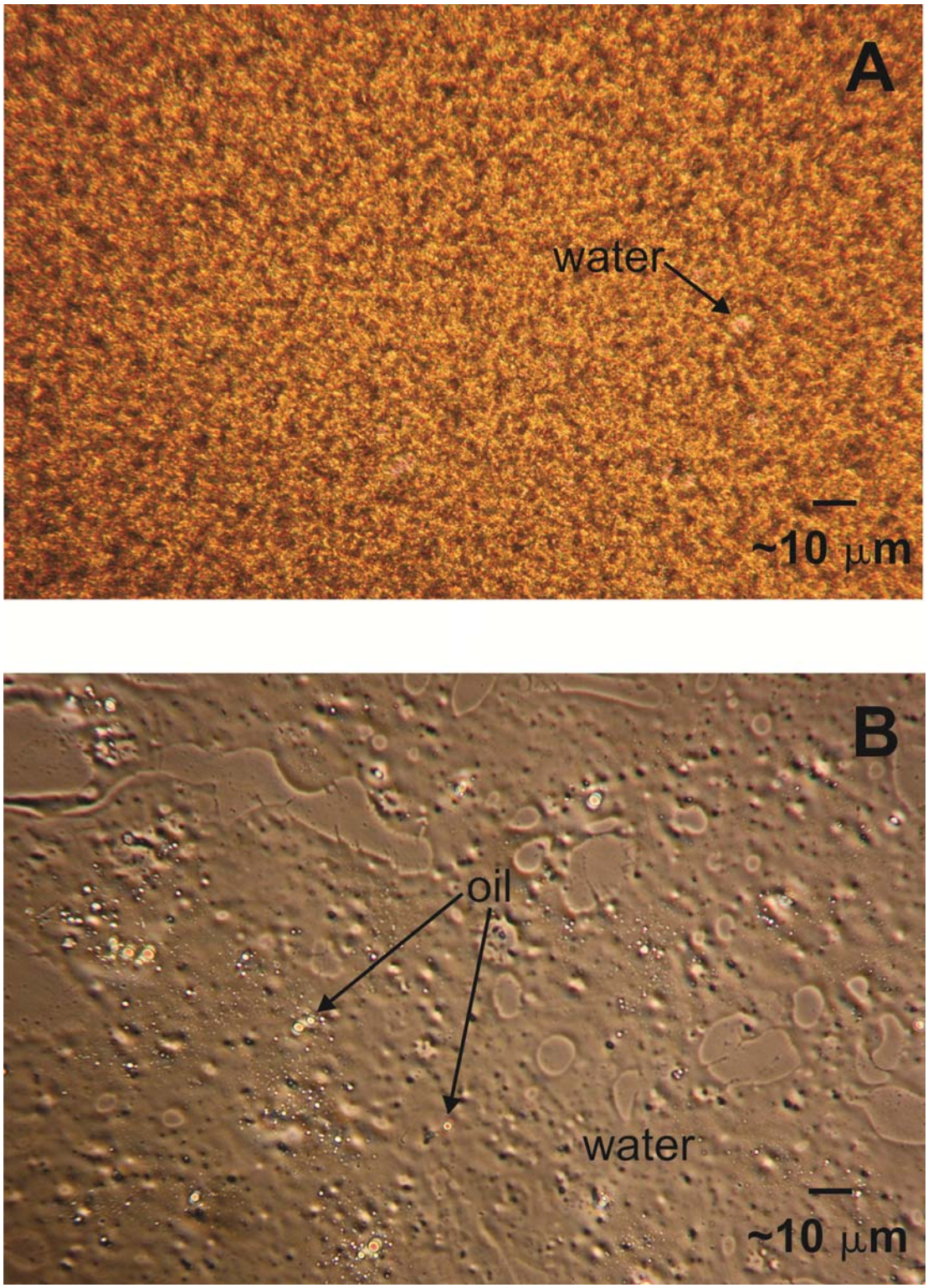

Figure 30. Clarified actual MC252 emulsion (A) and the aqueous solution resolved from this emulsion (B) under centrifugation (50% volume fraction octanol).

Conclusions

Our initial hypothesis was that the emulsion destabilizing properties of commercially-available oil dispersants can be enhanced by modifying the composition and fraction of polar constituents in the oil phase of W/O emulsions and increasing the pH of the emulsion aqueous phase. The results presented here suggest that emulsion stability is relatively insensitive to emulsion aqueous phase pH. Additionally, our results indicate that emulsion instability is appreciably enhanced as a consequence of treatment with Corexit modified with the polar additives octanol and hexylamine. Further, for octanol-modified or hexylamine-modified Corexit at 50% volume or greater octanol or hexylamine, the instability of the emulsion (with respect to reduced viscosity and enhanced weathering potential) appears to increase. Our current interpretation of this result is that changes at the oil-water interface favorable to the creation of a microemulsion are driving this phenomenon.

Our observations indicate that microemulsion formation reduces emulsion viscosity while increasing the ability of the emulsion to retain aqueous solution. Thus, although the ability to resolve water from emulsions treated with octanol- or hexylamine-modified Corexit (at 50% volume or greater octanol or hexylamine) under centrifugation is reduced, the transformation to a microemulsion and the decrease in apparent emulsion viscosity results a destabilized emulsion more amenable to physicochemical weathering and biological degradation (Lessard and DeMarco, 2000). Moreover, our experience working with actual MC252 emulsions have demonstrated that, as a result of their substantial viscosity, they are extremely difficult to recover by any means other than manually. This is true even for MC252 emulsions treated with Corexit. However, our results suggest that when Corexit is modified with octanol or hexylamine (at volume fractions approximately 40%-50%), the formation of a microemulsion reduces the viscosity of the emulsion to a degree that it may be recoverable by means other than manually (for example, oil skimmers and vacuum collection systems).

We are continuing our investigation into the behavior of W/O emulsions treated with modified commercially-available dispersants. Future studies will include experiments to examine the transition to microemulsion and the resulting decrease in emulsion viscosity, using actual

MC252 emulsions and focusing on octanol as the dispersant modifier. We will also continue our examination of other polar additives as possible dispersant modifiers. Our goal is to examine the practicality of this approach for favorably changing emulsion properties under real-world conditions.

References

Djuve J, Yang X, Fjellanger IJ, Sjöblom J, Pelizzetti E. Chemical destabilization of crude oil based emulsions and asphaltene stabilized emulsions. *Colloid & Polymer Science*. 2001; 279(3), 232-239.

Fingas M, Fieldhouse B. Studies on crude oil and petroleum product emulsions: Water resolution and rheology. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2009; 333, 67-81.

Fingas M, Fieldhouse B, Mullin J. Studies of Water-In-Oil Emulsions: The Role of Asphaltenes and Resins. In: *Nineteenth Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ontario, Canada*. 1996; 73-88.

Hayworth, J. S. Laboratory-scale investigation of a method for enhancing the effectiveness of oil dispersants in destabilizing water in oil emulsions. Draft Interim Report submitted to the Bureau of Safety and Environmental Enforcement, U. S. Department of Interior, Prepared under Contract E12PC00008, May 1, 2012.

Hazen, T. C., Dubinsky, E. A., DeSantis, T. Z., Andersen, G. L., Piceno, Y. M., Singh, N., Jansson, J. K., Probst, A., Borglin, S. E., Fortney, J. L., Stringfellow, W. T., Bill, M., Conrad, M. E., Tom, L. M., Chavarria, K. L., Alusi, T. R., Lamendella, R., Joyner, D. C., Spier, C., Baelum, J., Auer, M., Zemla, M. L., Chakraborty, R., Sonnenthal, E. L., D'haeseleer, P., Holman, H. N., Osman, S., Lu, Z., Van Nostrand, J. D., Deng, Y., Zhou, J., Mason, O. U. Deep-sea oil plume enriches indigenous oil-degrading bacteria. *Science*. 2010; 330(6001), 204-208, DOI: 10.1126/science.1195979.

Lessard, R. R., DeMarco, G. The Significance of Oil Spill Dispersants. *Spill Science & Technology Bulletin*. 2000; 6(1), 59-68, ISSN 1353-2561, 10.1016/S1353-2561(99)00061-4.

Martin, T. M., Young, D. M. Prediction of the acute toxicity (96-h LC50) of organic compounds to the Fathead Minnow (Pimephales promelas) using a group contribution method. *Chemical Research in Toxicology.* 2001; 14(10), 1378-1385.

Poteau S, Argiller J-F, Langevin D, Pincet F, Perez E. Influence of pH on Stability and Dynamic Properties of Asphaltenes and Other Amphiphilic Molecules at the Oil-Water Interface. *Energy & Fuels*. 2005; 19, 337-1341.

Sjöblom, J.; Söderlund, H.; Lindblad, S.; Johansen, E. J.; Skjärvö, I. M. Water-in-crude oil emulsions from the Norwegian continental shelf. *Colloid & Polymer Sci.* 1990; 268 (4), 389-398.

Sjöblom, J.; Aske, N.; Harald Auflem, I.; Brandal, Ø.; Erik Havre, T.; Sæther, Ø.; Westvik, A.; Eng Johnsen, E.; Kallevik, H., Our current understanding of water-in-crude oil emulsions.: Recent characterization techniques and high pressure performance. *Advances in Colloid and Interface Science.* 2003; 100–102, 399-473.

Wasan, D. T.; McNamara, J. J.; Shah, S. M.; Sampath, K.; Aderangi, N., The Role of Coalescence Phenomena and Interfacial Rheological Properties in Enhanced Oil Recovery: An Overview. *Journal of Rheology.* 1979; 23 (2), 181-207.