2015

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Recommended Citation

Loebig, Cameron Joseph, "Sinking of Crude Oil Amended-Model Oil Mixtures Due to Evaporative or Dissolution Weathering on the Surface and Submerged in Water" (2015). *LSU Master's Theses*. 3263.
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SINKING OF CRUDE OIL AMENDED-MODEL OIL MIXTURES DUE TO EVAPORATIVE OR DISSOLUTION WEATHERING ON THE SURFACE AND SUBMERGED IN WATER

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Chemical Engineering

by
Cameron Joseph Loebig
B.S., Louisiana State University, 2010
August 2015

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APPENDIX

ABSTRACT

Despite the popular belief that crude oil is a mixture of hydrocarbons that floats on the surface of water, tar balls continue to wash up on beaches from the sea floor years after the Deep Water Horizon oil spill. This is because of the rarely studied weathering effects that occur during deep sea spills. While the evaporative weathering process of oil at the water’s surface has been studied, no currently implemented models assess the weathering effects of dissolution within the water column. The evaporative effects at the sea surface and the dissolution of soluble components within droplets located in the water column leave a heavy fraction of oil that may sink. Laboratory experiments from previous work used hydrocarbon-like chemicals to form binary model oils. In contrast, experiments presented in this work use crude oil amended model oil (COA-MO) mixtures where the sinking of heavy fractions of crude oil does occur. The evaporative weathering binary model, when applied to COA-MO mixtures, was able to predict the sinking times of oil droplets using physical data of the three individual components of the mixture (crude oil, a light volatile, and heavy non-volatile chemical). The dissolution bonary model was able to predict the sinking times of COA-MO mixtures while submerged under water. A range of experimentally derived dissolution time constant, K, was obtained which could be applied to a broad spectrum of real world oils where the solubility of individual crude oil components varies greatly.

CHAPTER 1. Introduction

1.1 Introduction

With the ever increasing interest in deep water drilling, methods and models must be developed for the tracking of oil after deep sea spills. Deep sea spills are an inevitable reality that must be addressed in order to protect marine wildlife as well as industries that rely on healthy aquatic ecosystems. While surface spills have many models that effectively describe real world scenarios, there is a major gap in the current knowledge in the transfer and fate of oil in deep water settings (French, D. et al. 1996). Current models account for evaporation, diffusion driven entrainment, sub-surface currents, biodegradation, and other weathering effects; but often dissolution, as it contributes to the overall chemodynamics of the oil in the water column, is ignored (French, D. et al. 1996 and Thibodeaux, L. et al. 2011). With the Deep Water Horizon spill, oil components were found throughout the water column, from the surface to the sea floor (Lehr, et al. 2010, [18]). In previous work (Stevens, C. 2014), evaporation and dissolution weathering were studied experimentally. Evapo-Sink and Solute-Sink process concepts were modeled successful using binary or pseudo-component oil mixtures.

A binary component model consists of two mixtures. One mixture contains the light species that are volatile and soluble while the other mixture contains the heavy species that are essentially non-volatile and of low solubility. A pseudo-component is an artificially formulated chemical substance which represents a large number of hydrocarbons within a specific distillation cut temperature range. Several such artificial formulations, typically four to eight, are used to characterize crude oils (French, D. et al. 1996; Fan, T et al. 2002). A binary component model can then be defined based on the pseudo-components.

Previous pure component model oil mixture experiments, which gave reasonable agreements in predicting sinking time and oil density with model equations (Stevens, C. 2014), will be compared with crude oil amended-model mixtures experiments in this work. Since model oils were used in previous work, the characteristics of crude oils need to be cataloged both qualitatively and quantitatively; furthermore, assumptions need to be made and tested regarding the volatility and solubility of the real oil model mixtures.

1.2 Objective

The objective of this work is to develop a weathering model for crude oil spills at the sea floor, within the water column, and on the sea surface. Crude oils are composed of numerous hydrocarbons. Each component has properties of volatility and solubility which dictate the way weathering processes occur. The weathering processes of concern are the evaporation of the volatile hydrocarbon fraction and dissolution of the soluble hydrocarbon fraction. For certain crude oils, the processes may produce a heavy hydrocarbon fraction that may drift with the currents and slowly settle downward in the water column or rapidly sink toward the sea floor. A binary component theoretical weathering model developed and verified for the processes, using pure chemicals with oil-like properties, will be evaluated using crude oils. Such a model would provide a design tool that simulates the processes of evaporation and dissolution providing a means of forecasting the mass fraction produced from a crude oil spill on water or near the sea floor.

CHAPTER 2. Crude Oils and La Brea Tar

2.1 Introduction

Before any evaporative or dissolution models can be applied to real world crude oil spills, the model must be verified by experimentation in the lab. In this paper, three crude oils are used: 38º API, 26.5º API, and La Brea California tar. The crude oil will be added to a known quantities of a volatile model oil mixture to form a new test mixture. This mixture will be treated as a pseudo-component mixture composed of three substances. For example, a "dead" crude oil, a volatile chemical, and a nonvolatile chemical. A "dead" oil is the term used to characterize de-gassed oils produced in tanks, typically through a heater-treater process. In the binary model, $V_A[m^3]$ is the volatile component volume fraction and $V_B[m^3]$ is the nonvolatile component volume. This mixture of V_A and V_B is used to calculate the initial value of the state variable, X_o used in the theoretical model, where X_o is equal to V_{Ao} divided by $V_{B,}$ where V_{Ao} is equal to the initial volatile component volume. Similar volumes are used for the soluble and insoluble components involved with dissolution. Each pure or pseudo-component has its own density, molecular weight, vapor pressure, and water solubility. In previous work (Stevens 2014), the binary mixtures were composed of two pure component chemicals with known volatile or nonvolatile properties as well as known soluble and insoluble properties. This work will be extended for use of the binary model to crude oil as a component.

Before performing weathering experimentation, the physical properties of the crude oil components must be determined. Measurements of density and estimations of molecular weights are needed for modeling the behavior of the mixtures will be determined for each "dead" crude oil.

2.2 38ºAPI Oil

The 38ºAPI oil was obtained from Bosco Field in St. Landry, Louisiana on April 20, 2011. This crude oil has a hazardous rating equivalent to gasoline and has been stored in a one gallon gasoline container. The sample was taken from the on-site heater-treater assembly and reported to have no vapor chemicals present in the sample.

For crude oil the specific gravity can be calculated using equation 1 [6].

$$API\ gravity\ ° = \frac{141.5}{S.G.} - 131.5 \qquad 1)$$

Where: $API\ gravity\ °$= the reported API gravity (in this case 38°), S.G. = specific gravity of the oil. Assuming the specific gravity of water is 1.00 [g/mL], the S.G. of the oil is the relative density of the oil, ρ_{oil} [g/mL]. To ensure the API rating of the crude oil had not changed during its storage time, the density of this crude oil was measured directly using an 11.5mL pycnometer; see Appendix A for measurement data and procedure. Over eight trials the average density of the water (the experimental standard) was 1.009 ± .002 g/mL with an error of 0.2%. The 38ºAPI oil was measured resulting in an average density of 0.82 ± .01 g/mL with an error of 1.7%. This is near the calculated density of 0.835 g/mL from equation 1 which will be used in the model calculations.

The molecular weight of the oil was then determined by correlations based on the API of the crude oil. The correlation for molecular weight is given by equation 2 (Whitson, C.H. 1983.and Riazi, M.R. et al. 1980):

$$M.W. = \frac{(K_{wc} * \rho_{oil}^{.84573})^{6.58848}}{4.5579} \qquad 2)$$

Where: M.W. = average molecular weight of the mixture [g/mol], K_{wc}= Watson Characterization factor [unitless], ρ_{oil}= density of the oil [g/mL]. For 38ºAPI oil, the Watson Characterization factor (K_{wc}) was selected from tables as being 11.8 (Watson,et al.1933 and Watson,et al.1935) This resulted in a molecular weight of 198 g/mol.

The surface tension (σ dynes/cm) was estimated to be 30 dynes per centimeter for all COA-MO mixtures used. From previous work (Stevens, C. 2014), the surface tension measured for pure component binary mixtures had very large errors resulting in nearly 30% differences. However, the value centers on 30 dynes/cm and the overall contribution of the surface tension to model predictions is minimal. For this reason 30 dynes/cm with be used in modeling the pseudo-component binary mixtures with real oils.

2.3 26.5ºAPI Oil

The 26.5ºAPI oil was also obtained from Bosco Field in St. Landry, Louisiana on April 20, 2011. This oil also has a hazardous rating equivalent to gasoline and has been stored in a one gallon gasoline container. Samples were taken from a separate on-site heater-treater assembly and reported to have no vapor chemicals in the sample. Equations 1, 2, and similar correlations used for the 38ºAPI oil can be used to determine the physical properties of the 26.5ºAPI oil. The measured average density of the 26.5ºAPI oil is 0.903±.002 g/mL with an error of 2%. See Appendix A for data. This is near 0.896 g/mL calculated from equation 1. Using equation 2 and the Watson Characterization factor (K_{wc}) of 11.5 (Watson, et al.1933 and Watson, et al.1935), the calculated molecular weight of 26.5ºAPI oil was 163g/mol (Whitson, 1983.and Riazi, et al. 1980).

2.4 Tar

The tar used in these experiments was obtained from the La Brea tar pits in Los Angeles, California on July 9, 2014. The tar samples were obtained from a water runoff system during routine clearing maintenance of the pump system. Measurements with the pycnometer were again performed to obtain the density of the tar; it yielded inconsistent results ranging from 0.85-0.97 g/mL. Previous observations demonstrate that the density of this tar is great enough that a water layer exists on the surface of tar pools. The inconsistent density measurements with the pyconmeter were likely due to small air pockets trapped within the tar as it was injected into the pycnometer. Therefore, to better measure the density of tar, standard displacement methods were employed using a 50mL volumetric flask, deionized water, a syringe, and a large bore needle (see Appendix A for procedure). The measured density of tar by displacement was 1.002 g/mL which yielded 9.75ºAPI for tar. This La Brea tar which is a coal tar was compared to the coal tar analyzed in Hambly et al. 1998. Using the data from Hambly et al. 1998, it is estimated the molecular weight of the La Brea tar was 312.5g/mol.

Table 1 shows the physical properties of vapor pressure, density, and solubility for the pure components and the 38ºAPI oil, 26.5º API oil, and tar used in weathering experiments. For initial modeling purposes it is assumed that the crude oil components contribute to both the volatile and nonvolatile fraction in evaporation of the binary mixture. In dissolution it is also modeled as both the soluble and insoluble fraction. This assumption is tested against the experimental results. Also, in Table 1 are the molar densities of each substance. C_A is the concentration of the volatile and soluble component and C_B is the concentration of the nonvolatile and insoluble component. The reader should notice the last two columns. Column 8 list the single substances used for component A while column 9 lists the two substances used for component B.

Table 1. Physical and Chemical Properties of Model and Natural Oils Used in Experiments.

Mixture and Symbol	Species: Chemical or Natural Oil	Mol. Wt. [g/mol]	Mass Density [g/mL]	Vapor pressure @25ºC [atm]	Solubility in water @25ºC [mg/L]	Molar Density [mol/m^3]	Conc. C_A [mol/m^3]	Conc. C_B [mol/m^3] Crude Oil+ODB
Volatile or Soluble A	Benzene	78	.87	.132	1800	11221	11221	N/A
	Cyclohexane	84	.80	.128	55	9256	9256	N/A
	Hexane	86	.66	.202	9.5	7647	7647	N/A
Nonvolatile or Insoluble B *(UK= unknown)	Tar	313	1.002	UK	UK	3206	N/A	12055
	38 API	193	.84	UK	UK	4325	N/A	13175
	26.5 API	163	.90	UK	UK	5494	N/A	14344
	ODB	147	1.30	.002	140	8850	N/A	N/A

CHAPTER 3. Evaporative Weathering

3.1 Introduction

Crude oils can be composed of thousands of different components. These components can be separated into the SARA fractions of oils: saturates, aromatics, resins, and asphaltenes (Tianguang Fan, et al. 2002). Typically the saturates and aromatics make up a large portion of light hydrocarbons with high vapor pressures while the resins and asphaltenes have lower vapor pressures and lower solubility in water. For a surface spill of oil on water, the dominating weathering process is evaporation (French, D. et al. 1996). The lighter, higher vapor pressure components evaporate off the oil slick into the atmosphere leaving the heavier components behind (Speight, J. 1991). Should enough volatile material evaporate off the slick, the remaining oil may reach a density greater than the water lose its buoyancy resulting in sinking droplets (Wilson et al. 1986). In previous work (Stevens, C. 2014), binary mixtures of pure components were modeled and verified for the evaporative process. The binary pure-component Evapo-Sinking model was able to predict density changes of the slick and drop times of oil droplets accurately. In this study the model is extended to pseudo-component binary mixtures with three components where a mixture is composed of known volatile mixture of two components and an additional crude oil component. The crude oil component can be modeled as either contributing to the volatile fraction or nonvolatile fraction.

3.2 Theoretical Model

The Evapo-Sink experiments simulate a sea surface slicks. It will follow the behavior of sinking droplets where only one species (benzene, cyclohexane, or hexane) is treated as the volatile component A. Component B consists of two substances: ODB plus the crude oil species. Therefore, the A and B mixture can be considered a pseudo-binary system. See Stevens, 2014 or Appendix B for details on the basis for the Evapo-Sink Model. The equations used are:

$$\mathrm{Kt} = (X_o - \mathrm{X}\,(\mathrm{t})) + \left[\left(\frac{C_B}{C_A}\right) \ln \left(\frac{X_o}{\mathrm{X(t)}}\right)\right] \qquad 3)$$

$$K = \left(\frac{S}{V_{Bo}}\right) \left[\left(\frac{k_A \gamma_{Ao} p_A^*}{\mathrm{RT}C_A}\right) + \left(\frac{k_W \rho_W^*}{M.W._A C_A}\right)\right] \qquad 4)$$

Where: K=overall weathering coefficient [1/s], t=weathering time of the droplet, X_o= V_{Ao}/V_{Bo} (initial state variable), X(t)=$V_A(t)/V_{Bo}$ (state variable at time equal to t), C=molar density [mol/m^3] of either A or B, S= surface area of slick [m^2], k_A=air side mass transfer coeffiecient [m/s], γ_{Ao}=activity coefficient of species A, p_A^*=vapor pressure [atm] of component A, R=gas constant [m^3*atm/mol*K], T=temperature [K], k_W=water side mass transfer coefficient [m/s], ρ_W^*=solubility of A in water [g/L], M.W.$_A$=molecular weight of species A [g/mol]. Equation 3 is the main equation for tracking the density of the oil slick as a function of time with the state variable X(t). With initial volumes of each component in the mixture, X_o as well as C_A, and C_B are known at the starting time of the experiment at t=0.

Equation 4 gives the dissolution time constant in terms of volatile component properties on the water side and air side of the slick. Since evaporative weathering is dominated by evaporation on the air side of the slick (Thibodeaux, et al. 2011), we can assume the water side MTC is negligible, reducing Equation 4 reduces to

$$K_e = \left(\frac{K_A}{h_o}\right) \left(\frac{\gamma_{Ao} p_A^*}{\mathrm{RT}C_A}\right) \qquad 5)$$

Where K_e is the evaporative rate constant [s^{-1}], h_o is equal to the slick thickness of a surface water spill and K_A is equal to the overall mass transfer coefficient on the air side.

In order to model the time, t = τ, of a droplet sinking from the surface, the value of the state variable of the oil droplet at the critical density is needed. It describes the density in terms of the state variable at which the droplet has lost enough light, volatile material to be heavy enough to sink. It is given by equation 6.

$$X^* = (\rho_B^* - \rho_c) / (\rho_c - \rho_A^*) \qquad 6)$$

Where: X^*=volume fraction at critical density, ρ_B^*= density of non-volatile component [g/mL], ρ_A^*=density of volatile component [g/mL], and ρ_c=critical density [g/mL] and

$$\rho_c = \frac{6\sigma}{g} * \left(\frac{\pi}{6V_D}\right)^{\left(\frac{2}{3}\right)} + \rho_w \qquad 7)$$

Where: σ= oil-water interfacial tension [dyne/cm], g= acceleration due to gravity [cm/s^2], V_D= volume of the droplet [m^3], ρ_w= water density. Substituting the term X^* into Equation 4 yields:

$$K_e\tau = (X_o - X^*) + \left[\left(\frac{C_B}{C_A}\right) \ln \left(\frac{X_o}{X^*}\right)\right] \qquad 8)$$

Equations 5-8 are used as follows with experimental data and known parameters. The Sessile drop formula, Equation 7, provides the ρ_c value needed to calculate the critical state variable X^* in Equation 6. This is the numerical value of the state variable when oil droplets achieve a density of the surrounding water. At this time the droplet may break off from the slick and sink. This X^* value is dependent upon surface tension (σ) and droplet volume (V_D). The value of the air side MTC, K_A, is the one adjustable parameter in Equation 5. The value of the slick thickness, h_o, is obtained from V_{Bo}/S as given in Equation 4 or Appendix C. Experimental data is fit to the model, Equation 8, to obtain time constant, K. It can be used with Equation 5 to estimate the overall mass transfer coefficient, K_A, for each mixture.

3.3 Experimental Method

For the evapo-sinking process, experiments were conducted with either one benzene, hexane, or cyclohexane as the volatile components and ODB, combined with either 38º, 26.5ºAPI oil, or the tar as non-volatile components. Values of vapor pressure for pure component chemicals listed in Table 1 were taken from Green, et al. 2008. The volatile components were chosen based on previous work in our laboratory (Stevens 2014) where they were successfully modeled as binary mixtures which the non-volatile fraction was only ODB. The volume of each substance was chosen to make the initial mixture density fall within the 0.91-0.99 g/mL range. Although ODB is semi-volatile, its vapor pressure is much lower than the volatile species used and can be considered a non-volatile component (Stevens, 2014). Mixtures were prepared in 100mL volumetric flasks and assumed to have ideal mixing behavior; the volume fractions are used to obtain the total mixture volume. These mixtures are listed in Appendix C.

The evapo-sink test apparatus used were two 36L cylindrical jars filled with fresh water and placed under a laboratory fume hood with an air velocity of 80 [ft/s]. Non-detect readings from the anemometer placed at the water surface indicated air directly above the oil slick is not well circulated and near stagnant. Between experiments the jars were cleaned of residual oil using toluene, allowed to dry, and refilled with fresh water. The fresh water was allowed to sit overnight and reach room temperature (27 ± 1 °C or ~300K). Initial slick thicknesses were determined by photographing the surface area coverage of a slick occupied by a known volume of oil mixtures: see experimentally details in Appendix C). Sinking times were recorded with a stop watch. The time period between the times the oil mixture was poured to the time the droplet fell defines τ [min], the sinking time. A volumetric pipette was used to obtain a sample the oil on the bottom of the jar. The density of the oil was measured using a 1mL volumetric flask and a Mettler Toledo (AB104) balance. A total of 54 Evapo-sink experiments were performed using nine different COA-MO mixtures. The observed τ and oil droplet density were recorded for each experiment.

3.4 Results

The following describe the observed evapo-sinking process. At the beginning of an experiment, 50mL of oil mixture were poured onto the water surface to form a floating oil slick. As the evaporative weathering process proceeded and light volatiles were lost, the slick began to sag downward until the oil's critical density was reached. When the interfacial tension between the oil and water was overcome and the oil droplet broke off from the surface under the slick, the oil droplet settled to the bottom of the jar. Figures 1-A,B,and C show the first oil droplet forming and cleaving from the surface slick. This is the expected behavior of the oil during the evaporative weathering process. Table 2 contains the measured and calculated parameters for each experiment.

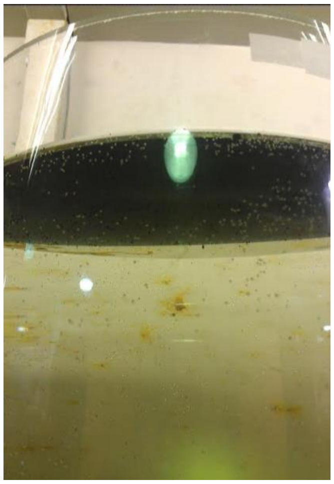

Figure 1-A. Initial slick of benzene/tar/ODB

Figure 1-B. Slick sags down after lighter volatile components evaporate

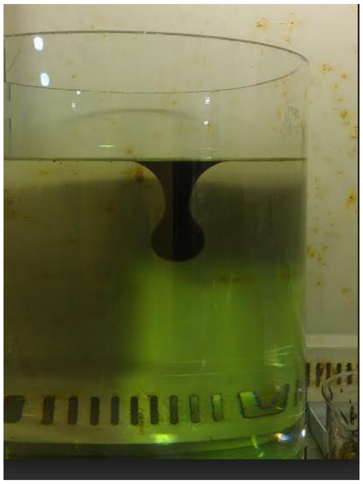

Figure 1-C. Droplet breaks off from slick and falls to bottom of jar.

Table 2: Measured and Model-Estimated Parameters for Crude Oil Amended –Model Oil Mixtures Evaporation-Sinking Experiments.

ROA-MO mixtures	**# of trials**	**Initial X_o**	**Initial ρ of slick [g/mL]**	**Drop time [min]**	**Critical ρ [g/mL]**	**K_A [m/min] Mass tr. coeff.**
		Measured	Calculated	Measured	Measured	Model fit
Benzene/tar/ODB	6	2.33	0.97	10.6 ± 0.9	1.029 ± .003	.088
cyclohexane/tar/ODB	6	1.22	0.97	6.5 ± 0.9	1.015 ± .009	.05
hexane/tar/ODB	6	1.00	0.92	6.8 ± 0.4	1.05 ± .04	.084
Benzene/38API/ODB	6	0.30	0.98	21.5 ± 0.6	1.016 ± .007	.043
cyclohexane/38API /ODB	7	0.67	0.95	15 ± 1	1.04 ± .01	.062
hexane/38API /ODB	6	0.67	0.90	8.3 ± 0.6	1.048 ± .007	.086
Benzene/26.5API/ODB	6	0.67	0.97	13 ± 1.5	1.012 ± .007	.08
cyclohexane/26.5API /ODB	6	0.67	0.97	8.9 ± 0.9	1.04 ± .01	.062
hexane/26.5API /ODB	5	0.67	0.92	5.6 ± 0.4	1.042 ± .009	.08

Volatile benzene, non-volatile tar and ODB mixtures yielded average sinking times of 10.6 minutes with an 8% error. Volatile cyclohexane and hexane mixtures with the same non-volatile components yielded average sinking times of 6.5 and 6.8 minutes with 13% and 6% error respectively.

Volatile benzene, non-volatile 38API, and ODB mixtures yielded an average sinking time of 22 minutes with an error of 3%. Volatile cyclohexane and hexane mixtures with the same nonvolatile components yielded average sinking times of 15 and 8 minutes with 7% and 9% error respectively.

Volatile benzene, non-volatile 26.5°API, and ODB mixtures yielded an average sinking time of 13 minutes with an error of 11%. Volatile cyclohexane and hexane mixtures with the same nonvolatile components yielded average sinking times of 9 and 6 minutes with 10% and 7% error respectively. Model fit calculations of, K_A, the overall evaporative MTC all fell within 0.04-0.09 [m/min] and are of the same order of magnitude; see Table 2.

In all cases hexane, with the highest vapor pressure, had the shortest drop times. Benzene had the longest drop times and a low vapor pressure. Likewise, cyclohexane, except for the case where tar was present in the mixture, also had long drop times; it also has low vapor pressure. See Table 1 for vapor pressure values. The value of the critical droplet density range from 1.01 to 1.05 [g/mL] and appear independent of the density of the non-volatile oil or tar.

The solid lines in Figures 2-4 show the calculated density of the oil slick over time using theoretical model equations 5 and 8. A single model calculation was performed for each set of experiments using its average K_A value appearing in Table 2. The recorded data points for each graph fall in line with the projected terminal time and density predicted by the model. A single line traces the slick density progression with the dissolution time, $[t, \rho(t)]$. It represents the average behavior of the data points in each experiments.

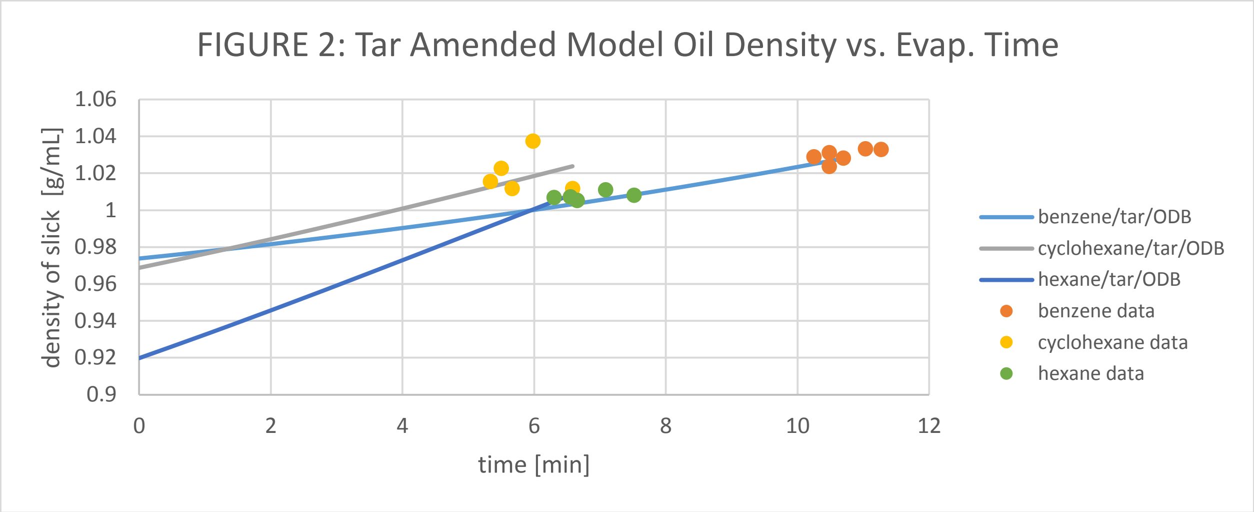
FIGURE 2: Tar Amended Model Oil Density vs. Evap. Time

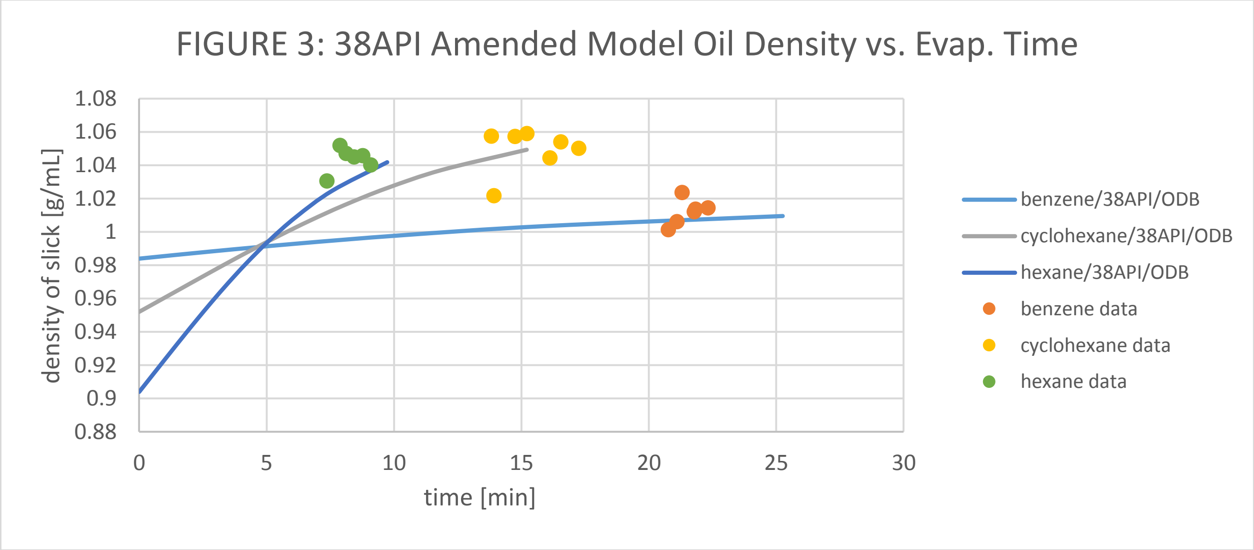
FIGURE 3: 38API Amended Model Oil Density vs. Evap. Time

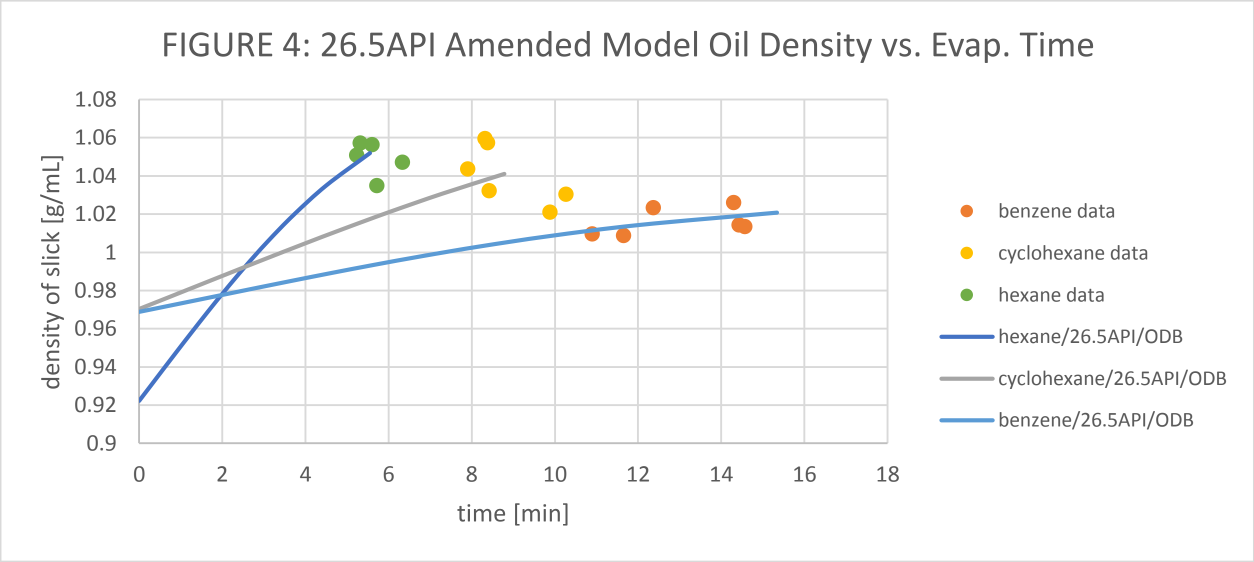
FIGURE 4: 26.5API Amended Model Oil Density vs. Evap. Time

Figures 2-4. Density vs. Evaporation Time

3.5 Discussion

Table 3 compares the K_A value of COA-MO mixtures from this work to the previous work of Stevens (2014). In previous work, binary pure component mixtures of benzene/ODB, cyclohexane/ODB, and hexane/ODB were used. Experimental mixtures used in this work are a combination of the binary pure component mixtures plus a crude oil species.

TABLE 3: Comparison of binary model-extracted evaporation MTCs K_A values for model oil mixtures.

Mixture	**K_A [m/min]** Model fit	**Mixture** *Stevens,2014	**K_A [m/min]** Model Fit from *Stevens, 2014
:Benzene/tar/ODB	.088	Benzene/ODB	.043
cyclohexane/tar/ODB	.05	Cyclohexane/ODB	.062
hexane/tar/ODB	.084	Hexane/ODB	.06
Benzene/38API/ODB	.043	Benzene/ODB	.043
cyclohexane/38API /ODB	.062	Cyclohexane/ODB	.062
hexane/38API /ODB	.086	Hexane/ODB	.06
Benzene/26.5API/ODB	.08	Benzene/ODB	.043
cyclohexane/26.5API /ODB	.062	Cyclohexane/ODB	.062
hexane/26.5API /ODB	.08	Hexane/ODB	.06

The K_A values of this work compared to previous work of Stevens (2014) are the same order of magnitude and in some cases exact matches. The K_A value of this work range from 0.043-0.088 [m/hr]. In previous work (Stevens, 2014), the K_A values range from 0.043-0.062 [m/hr]. This supports the idea that crude oil mixtures may be modeled as a binary component system. However, this similarity in K_A values may be attributed to the real oil components being "dead" oils (i.e. oils that have no volatile components). The 38° and 26.5°API oils were reported to be free of volatile components upon receiving the sample material; and the tar, which had been exposed to the atmosphere for an unknown but extremely long period. Therefore, it could safely assumed to be without significant volatile components. In this case, modeling the pseudo-component crude oil as contributing to the non-volatile volume fraction is the logical choice. With this in mind, the experiments performed were similar to that of Stevens (2014) in that there was only one volatile component involved which drives the evaporative weathering process. Therefore, the similarities in the K_A values for both sets of experiments can be attributed to the same volatile component being present and evaporating off the surface slick. Likewise, the small differences in the K_A values may be attributed to either experimental constraints of the apparatus or interactions between the non-volatile "dead" crude oil component and the hydrocarbon-like chemicals used exclusively by Stevens (2014). The results presented indicate the two "dead" crude oils and tar behave as non-volatile constituents within the nine COA-MO mixtures used in the evapo-sink experiments.

3.6 Conclusion

COA-MO and model oil mixtures were modeled using a volatile volume fraction and a non-volatile volume fraction. Three know volatile hydrocarbons (benzene, cyclohexane, and hexane), one known non-volatile hydrocarbon (ortho-diclorobenzene), and three crude oils (tar, 38API, and 26.5API) were used. The experimental results were similar specifically in the qualitative visual aspect of the evapo/sinking process but also in the numerical convergence of the measured and model-produced parameters. The theoretical model was able to predict the weathering effects of evaporation of surface slicks when the crude oils were treated as non-volatile components. The overall mass transfer coefficients were comparable to binary model oil overall mass transfer coefficients presented in previous work (Stevens, 2014). This study demonstrated the physico-chemical properties of crude oil mixtures within the framework of a binary system model. This in turn implies that multi-component systems of crude oils, containing thousands of individual chemicals, may be modeled to provide an estimate of oil fractions produced and sinking times of droplets from an oil slick, however further work is needed. Crude oils behave similarly to pure chemicals used as model oils for the evaporation/sinking process, provided they are part of the non-volatile component of the binary system. This work focused on crude oils that had no significant volatile components; whether it may be applied to crude oils with volatile components is an open question.

CHAPTER 4. Dissolution of COA-MO mixtures.

4.1 Introduction

Dissolution of the solutes from within the oil droplets is an important weathering factor when considering deep sea spills (Thibodeaux, 2012; Federal Interagency Solutions Group, 2010). As oil droplets travel up the water column towards the sea surface, soluble components may dissolve into the surrounding water through the droplet's outer surface area. This causes the density of the oil droplet to increase, which in turn slows the velocity of the droplet moving towards the sea surface. The density may then continue to increase to a point where the droplet becomes neutrally buoyant with the surrounding fluid. Eventually, if the density increases further, the droplet will begin to sink downward in the water column and move toward the sea floor. Smaller droplets of oil have a longer residence time submerged in the water column due the slow rise velocity with respect to droplet diameter (Welty et al., 2009). These smaller oil droplets are also more susceptible to dissolution weathering because the rate of solubilization will increase with the larger surface area to volume ratio (Thibodeaux, 2012). For these reasons it is suspected that plumes of oil observed at depth after the Deep Water Horizon spill in 2010 are due to the use of dispersants (Federal Interagency Solutions Group, 2010). These dispersants minimized the interfacial tension of the oil at the spill causing oil droplets to break up into smaller droplets. These droplets with small diameters, slow rise velocities, and large residence time were able to dissolve to a point that they remained suspended in the water column indefinitely (Federal Interagency Solutions Group, 2010).

In order to accurately track oils after a deep sea spill occurs, a model must be able to predict the dissolution weathering process of oil droplets within the water column. In previous work (Stevens, 2014) a solute-sink model was able to predict the behavior of binary model oils submerged in water. The solute-sink model presented in the following sections will highlight key factors and parameters needed to predict the dissolution of model oils containing a dead crude oil as a component of the mixtures undergoing dissolution.

4.2 Theoretical Model

The real model oils used in these experiments consist of a mixture of three substances: a soluble chemical, an insoluble chemical, and a crude oil. Tertiary mixtures were made volumetrically with V_A, the soluble component which changes with respect to time, and $V_{B,}$ the insoluble volume component, which remains constant with time. Both cases assume ideal mixing rules. The crude oil components of tar, 38ºAPI and 26.5ºAPI oil may be modeled as either a part of the soluble or insoluble component of the binary mixture. Initially, the real oil components are modeled as contributing to the insoluble volume. V_A plus V_B may be added to yield the total droplet volume V(t). The sum of $V_A(t=0)$ and V_B gives the initial volume, V_o. The state variable of the binary system, X(t), is defined as the ratio of the $V_A(t)$ to V_B at any time "t". The concentrations of the soluble species A and the insoluble species B in the droplet are: $\rho_A(t) = (\rho_A^* X(t))/(X(t)+1)$ and $\rho_B(t) = \rho_B^*/(X(t)+1)$. The ρ_A^* and ρ_B^* are the density of the components A and B respectively. As X(t) decreases with time the concentration of A in the oil droplet will decrease until the point that the mixture is of the same density as water, ρ_w. At this point the droplet will be neutrally buoyant; and should it be subject to further dissolution, the droplet will sink. As the concentration of A in the submerged droplet decreases, the X(t) will decrease from $X(t=0) = X_o$ to $X(t=\tau) = X^*$, where τ is the drop time and X^* is the soluble to insoluble volume ratio of the droplet at neutral buoyancy. Mass lost from the droplet will also decrease the diameter and surface area of the droplets with respect to time. These changes can be assessed using the state variable X(t) as follows: $d(t) =[(X(t)+1)/(X_o+1)]^{1/3}d_o$ and

$A(t)=\pi d_0^2[(X(t)+1)/(X(t)+1)]^{2/3}$, where d_o is the initial droplet diameter and A(t) is the surface area that changes with respect to time. Stevens (2014) further develops the model (Appendix D) where the model equations are:

$$K_s * \tau = \int \frac{(X(t)+1)^{\left(\frac{1}{3}\right)}}{X(t)} d(X(t)) \tag*{9)}$$

$$K_s = \frac{6 * K_W * (X_o+1)^{\left(\frac{1}{3}\right)}}{K_{ow} * d_o} \tag*{10)}$$

Equation 9, when integrated for an experimental value of τ will yield K_s, the dissolution rate constant [hr^{-1}] for each mixture. Theoretically, these overall dissolution time constants, K_s, are a function of the overall mass transfer coefficient (K_W), solute solubility (ρ_w^*), and the molecular weight (M.W.) of the solute. The other terms including droplet diameter (d_o) vary little between experiments. Values of K_W, partitioning coefficient (K_{ow}), and K are assumed constant.

4.3 Experimental Method

Nine mixtures containing the soluble chemicals (benzene, toluene, and 1-clorobutane), insoluble chemicals (ODB and 1-cloronaphthalene), and crude oils (tar, 38°API, and 26.5°API oil) were used. These were chosen based on their properties listed in Table 4. The crude oils are "dead" oils and have insignificant vapor pressure. UK means unknown value, but is assumed insignificant. The mixtures were made by combining the components on a volume basis producing a droplet with density between 0.97 and 0.99 g/mL. The volume fractions for each mixture appear in Table 5. Initial densities were designed to be near 1.00g/mL to ensure the loss of a small quantity of A would achieve a neutral droplet density quickly with a short dissolution time τ. The initial volume fractions of each component in the mixture, the initial state variable

X_o, and the density and diameter of the droplet can be calculated for each mixture. The data is reported in Table 6.

TABLE 4: Physical Properties of Components for Dissolution Weathering

Component	**V.P. [atm]**	**Solubility [mg/L]**	**M.W. [g/mol]**	**denisity [g/mL]**
benzene	0.142	1800	78.11	0.876
toluene	0.043	470	92.14	0.864
1-clorobutane	0.135	370	92.57	0.89
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ODB	0.002	156	147.01	1.301
1-cloronaphthalene	0.00004	17	162.62	1.194
tar	UK	UK	312.5	1.002
38 API	UK	UK	193	0.835
26.5API	UK	UK	163	0.896

TABLE 5: Volume Percentage of Individual Components of COA-MO Mixtures

	Component and Volume percentage							
Mixture:	benzene	toluene	1-cloroB	ODB	1-cloroN	tar	26.5API	38API
Benzene/ODB/Tar	50%	0	0	13%	0	37%	0	0
Tolene/1-cloroN/Tar	0	40%	0	0	18%	42%	0	0
1-cloroB/1-cloroN/Tar	0	0	55%	0	25%	20%	0	0
Benzene/ODB/26.5API	35%	0	0	25%	0	0	40%	0
Tolene/1-cloroN/26.5APIAPI	0	40%	0	0	37%	0	23%	0
1-cloroB/1-cloroN/26.5APIAPI	0	0	40%	0	34%	0	26%	0
Benzene/ODB/38API	40%	0	0	30%	0	0	0	30%
Tolene/1-cloroN/38API	0	29%	0	0	41%	0	0	30%
1-cloroB/1-cloroN/38API	0	0	32%	0	38%	0	0	30%

TABLE 6: Initial conditions of COA-MO mixtures

Tar	X_O	ρ_0 [g/mL]	V_o [mL]	d_o [cm]
benzene/ODB/tar	1.00	0.978	20	3.37
toluene/1-cloronaphthalene/tar	0.67	0.981	10	2.67
1-clorobutane/1-cloronaphthalene/tar	1.22	0.988	15	3.06
38API				
benzene/ODB/38API	0.67	0.991	15	3.06
toluene/1-cloronaphthalene/38API	0.41	0.991	15	3.06
1-clorobutane/1-cloronaphthalene/38API	0.47	0.989	15	3.06
26.5API				
benzene/ODB/26.5API	0.54	0.990	15	3.06
toluene/1-cloronaphthalene/26.5API	0.67	0.993	15	3.06
1-clorobutane/1-cloronaphthalene/26.5API	0.67	0.995	15	3.06

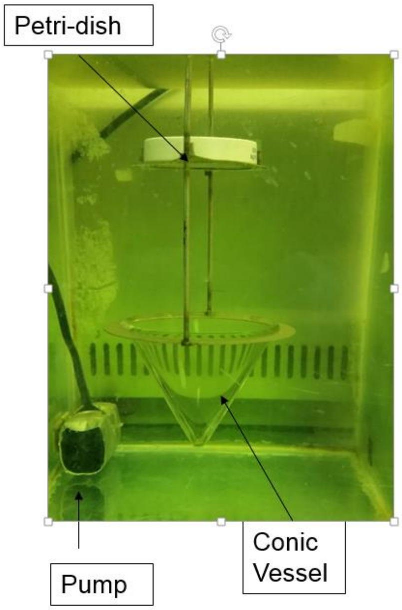


Figure 5: Apparatus for Dissolution Experiments

The experiments were conducted in 45L tanks filled with fresh water. The water was allowed to reach room temperature overnight after cleaning. An apparatus composed of a metal frame that retained an inverted petri dish and a glass cone to catch falling droplets (see Figure 5) was used to keep the oil droplet submerged under water and off the surface during the experiment. Droplets of volume 10mL-20mL were injected using a 20mL polyethylene syringe and tubing under the petri dish. An Aqueon Circulation Pump 500 (500gal/hr) was placed on the bottom left-hand side of each tank and secured with Velcro to ensure that similar circulation patterns occurred in all tanks. A video camera was set up to record the times, τ, at which the sinking droplets occurred. After the droplets fell, the volumes were obtained and samples were retrieved from the glass cone and density measurement were taken using a 1mL volumetric flask and a Mettler Toledo (AB104) balance.

4.4 Results

Droplets produced from the nine COA-MO mixtures fell at dissolution times varying from 23 to 151 hours. A droplet sinking event is captured and appears in Figure 6. From the experimental time, τ, for falling droplets, the overall dissolution time constant, K_s, was calculated using the model Equation 9. Key measured and calculated results in the model appear for each individual mixture were the crude oil was modeled as insoluble in Table 7.

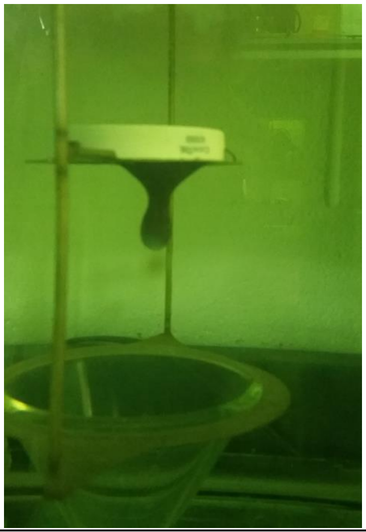


Figure 6: Psuedo-component crude oil droplet about to sink into cone shaped vessel due to dissolution

TABLE 7: Dissolution Data with the Crude Oil as Insoluble Component in the Model Mixture.

	X_o	X^*	ρ_o [g/mL]	time [hrs]	K_s [1/hr]
Tar					
benzene/ODB/tar	1	0.64	0.978	56± 9	0.0096
toluene/1-cloronaphthalene/tar	0.67	0.44	0.986	151 ± 17	0.0032
1-clorobutane/1-cloronaphthalene/tar	1.22	0.99	0.988	77 ± 4	0.0034
38API					
benzene/ODB/38API	0.67	0.55	0.991	24 ± 2	0.0095
toluene/1-cloronaphthalene/38API	0.41	0.31	0.991	94 ± 17	0.0029
1-clorobutane/1-cloronaphthalene/38API	0.47	0.32	0.989	73 ± 4	0.0057
26.5API					
benzene/ODB/26.5API	0.54	0.41	0.990	41 ± 5	0.0075
toluene/1-cloronaphthalene/26.5API	0.67	0.59	0.993	30 ± 3	0.0049
1-clorobutane/1-cloronaphthalene/26.5API	0.67	0.59	0.995	23 ± 6	0.0064

Being “dead” crude oil it is reasonable to assume this material is in fact a legitimate insoluble component in the mixture. It is treated so in the model and the dissolution time constant, K_s, is obtained for each experiment. The results appear in Table 7. However, there is no experimentally measurable evidence to demonstrate it is non-soluble. Mathematically it may also be modeled as a soluble material and be included as a part of component A even though it likely has zero vapor pressure. This has been done and the parameter, K_s, was obtained for each mixture where the crude oil was modeled as a soluble component. Calculated results were also generated using the same experimental data but assuming the crude oil was a soluble component in the model equation. They appear in table 8.

TABLE 8: Dissolution Data with the Crude Oil as Soluble Component in the Model Mixture.

	X_O	X*	ρ_o [g/mL]	Time [hrs]	K_s [1/hr]
Tar					
benzene/ODB/tar	6.69	4.27	0.978	56± 9	0.0145
toluene/1-cloronaphthalene/tar	4.56	2.96	0.981	151 ± 17	0.0047
1-clorobutane/1-cloronaphthalene/tar	3.00	2.42	0.988	77 ± 4	0.0043
38API					
benzene/ODB/38API	2.33	2.12	0.991	24 ± 2	0.0058
toluene/1-cloronaphthalene/38API	1.44	1.29	0.991	94 ± 17	0.0016
1-clorobutane/1-cloronaphthalene/38API	1.63	1.42	0.989	73 ± 4	0.0026
26.5API					
benzene/ODB/26.5API	3.00	2.65	0.990	41 ± 5	0.0047
toluene/1-cloronaphthalene/26.5API	1.70	1.56	0.993	30 ± 3	0.0039
1-clorobutane/1-cloronaphthalene/26.5API	1.94	1.80	0.995	23 ± 6	0.0046

In both Tables 7 and 8, the state variable, X, is seen to decrease from the initial value, X_o, to X^*. This indicates that dissolution of the soluble fraction has occurred, at which point droplet density exceeds that of water.

Table 9 show the values of K_s for mixtures containing the individual pure component soluble species in the COA-MO mixture as well as the K_s value for the combined soluble components. These numerical values of K_s differ somewhat as the crude oil component is modeled as contributing to either the soluble or insoluble fraction.

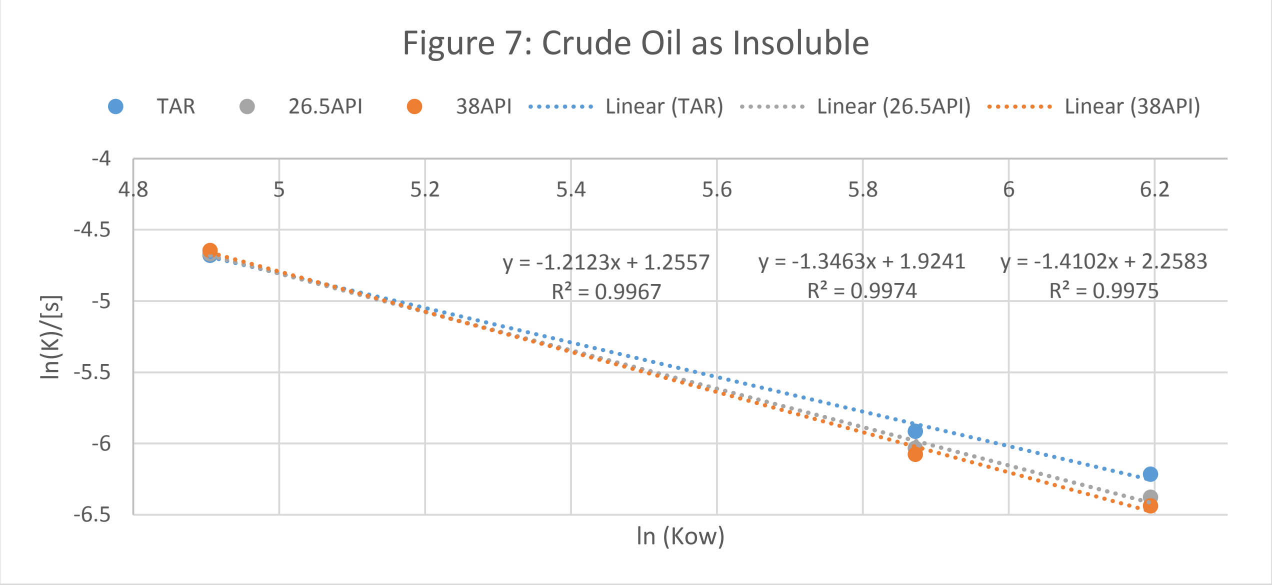
TABLE 9: Dissolution Time Constant, K_s, Data with the Crude Oil as Soluble or Insoluble.

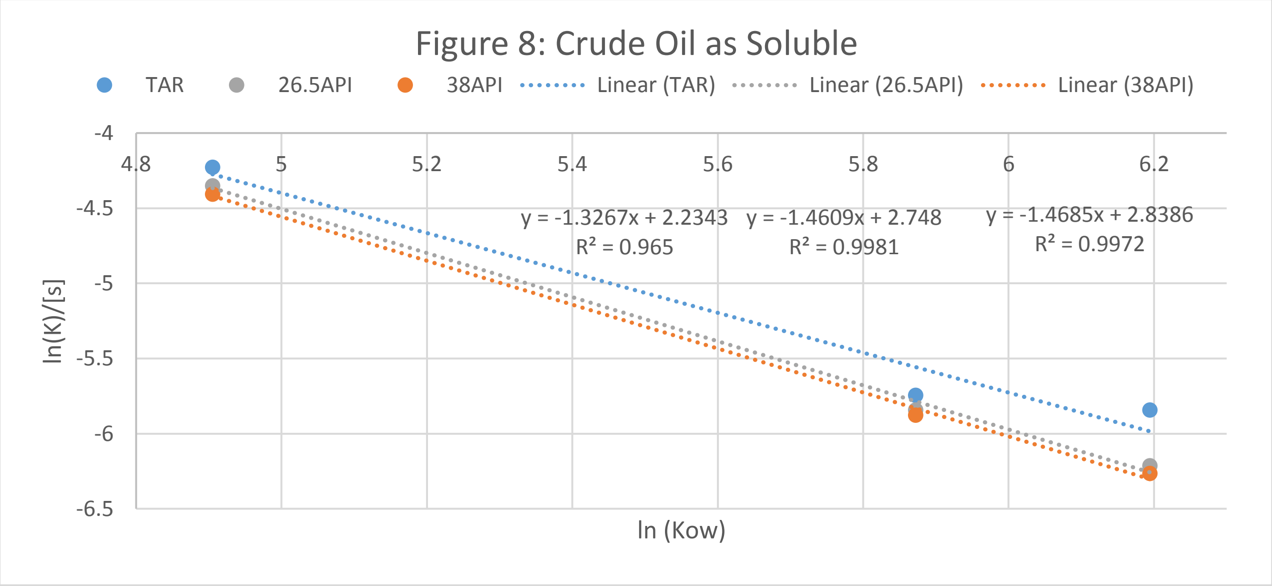
Soluble Component	Crude as SOLUBLE		Crude as INSOLUBLE	
	K_s [1/hr]	COV	K_s [1/hr]	COV
Benzene	0.008 ± 0.004	53%	0.009 ± 0.001	11%
Toluene	0.003 ± 0.001	40%	0.004 ± 0.001	25%
1-clorobutane	0.004 ± 0.001	24%	0.005 ± 0.001	25%
Overall:	0.005 ± 0.004	67%	0.006 ± 0.002	41%

4.5 Discussion

For mixtures containing benzene, the coefficient of variance (COV) of K_s is smaller when the dissolution is modeled with the crude oil component contributing to the insoluble fraction. However, toluene has a smaller COV when the crude oil is modeled as contributing to the insoluble fraction. Mixtures containing 1-clorobutane have nearly identical COV values when the crude oil is modeled as contributing to either the soluble or insoluble fraction. Overall, when the solute values are combined, the crude oil modeled as contributing to the insoluble fraction has a lower COV. In summary, there is no clear outcome as to whether the crude oil should be modeled as contributing to the soluble or insoluble fraction in the mixture. The truth likely lies somewhere in between.

Tables 7, 8, and 9 have large deviations and COVs associated with the overall average of the dissolution time constant, K_s. This is largely due to the difference in solubility of the hydrocarbon components of benzene, toluene, and 1-clorobutane, and to a lesser extent the crude oils. Benzene has a much greater solubility (illustrated in table 6) than the other two soluble hydrocarbons. In fact, the solubility of the soluble hydrocarbons is inversely proportional to the partitioning coefficients used, as indicated in Equation 10. The solubility of benzene, toluene,





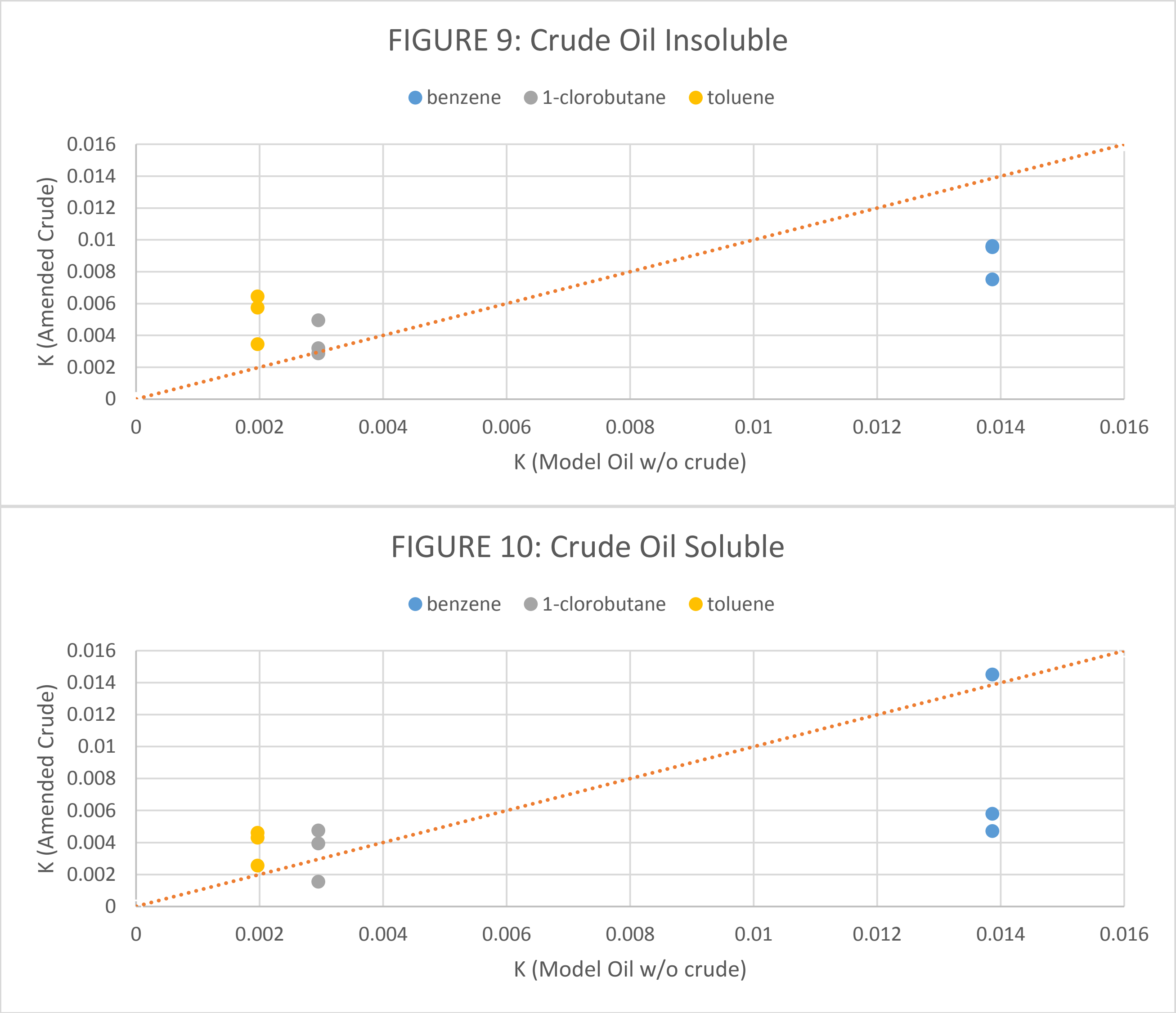
Figures 7 and 8. ln(K) vs. ln(K_{ow})

and 1-clorobutane are inversely proportional to the oil-to-water partitioning coefficient, K_{ow}. Values for the hydrocarbons are 135, 490, and 355 [m^3/m^3] respectively (Sangster, 1989).

Figures 7 and 8 graph the logarithmic relationship between the $\ln(K_s)$ and $\ln(K_{ow})$; this procedure is consistent with their theoretical functionality on Equation 10 and is appropriate for the crude oil modeled as either an insoluble or a soluble component of the mixture. Both figures show an increase in the value K_s with decreasing value of K_{ow} as suggested by the theory. In all cases, the slope of the linear fit for the data is nearly identical. However, the values of K_s overlap regardless of whether the crude oil is modeled as a soluble or insoluble fraction.

Taking the larger deviations of K_s from table 9 ($K=0.005 \pm 0.004$) gives a working approximation for a range of K_s where large differences in solubility between components occur.

While it has been demonstrated that the COA-MO mixtures can be modeled as having the crude oil component as either soluble or insoluble, each mixture is more accurately described using one model. Some of these mixtures are more easily modeled as though the crude oil component is soluble and some more easily modeled as though the crude oil component is insoluble. For this reason it is useful to compare the results of this work's experiments to previous work (Stevens, 2014), where binary model oils with the same hydrocarbon components used in the COA-MO mixtures were also used. Using the overall mass transfer coefficient, K_W; and the partition coefficient, K_{ow}; the initial state variable, X_o; and droplet diameter, d_o, from Stevens (2014); Equation 10 can be used to calculate the dissolution time constants, K_s, for this previous work. The binary pure component mixtures used by Stevens (2014) were:



Figures 9 and 10. K Amended Crude vs. K Model oil

benzene/ODB, 1-clorobutane/1-cloronapthalene, and toluene/1-cloronapthalene. These mixtures had dissolution time constants, K, of 0.014, 0.003, and 0.002 respectively. The values of the dissolution time constants, K_s, from this work and Stevens (2014) work can be plotted one to one against each other. Figures 9 and 10 shows the one to one correspondence of the K_s values where the crude oil is modeled as insoluble and soluble component respectively. In the cases where the data points fall on or near the diagonal center line, the experimental K_s values are in agreement and the presence of the crude oil is inconsequencal. In some cases it is clear that certain data points fall away from the center line. This indicates the crude oil component has an effect on the dissolution weathering process. In some cases the crude oil component appears to be modeled more accurately as an insoluble component as in the case of benzene containing mixtures. Overall, the three mixtures containing benzene are closer to the center line when the crude oil is modeled as insoluble. This could largely be due to the fact that benzene has a high solubility in comparison to other components in the mixture and therefore is the main driving force in the mass transfer of material out of the submerged droplet. By comparing the K_s values for each COA-MO mixture to the corresponding K_s value for the pure component binary mixture form previous work, the contribution of the crude oil to mass transfer can be estimated. If the K value of the COA-MO mixtures is close to the K value of the binary model oil mixtures, the COA-MO mixture is better modeled as having the crude oil component partitioned in the insoluble volume fraction. For example the mixture of toluene/1-cloronapthalene/38ºAPI from this work has K_s values of 0.0029 for crude oil as insoluble and 0.0016 for crude oil as soluble (see tables 7 and 8). The binary model oil from previous work of toluene/1-cloronapthalene has a K_s value of 0.002. In this case the COA-MO mixture of toluene/1-cloronapthalene/38ºAPI, this mixture should be modeled with the crude oil component as soluble.

Table 10 shows the final analysis of the nine COA-MO mixtures used in this experiment with initial conditions, droplet sink times, and overall dissolution time constants. If the K_s values of the crude oil mixtures when compared to the K_s of the model oil mixtures were similar, the data from Table 7. Otherwise data from Table 8 was used. COA-MO mixtures containing the crude oil component of tar were more accurately modeled with the tar as an insoluble component. Based on the physical properties of tar, this is not surprising. Tar has been long known to be composed of heavy insoluble materials. COA-MO mixtures containing benzene were also more accurately modeled as having the crude oil as an insoluble component because of the high solubility of benzene. While it is possible that the 26.5ºAPI and 38ºAPI oils had some soluble fraction, when compared to benzene the crude oils are at least an order of magnitude less soluble. COA-MO mixtures containing toluene or 1-cloronapthalene with either 26.5ºAPI or 38ºAPI crude oil yielded K_s values suggesting the crude oil component contributed to dissolution weathering.

TABLE 10: Experimental data of COA-MO mixtures

	X_o	X^*	ρ_o	Time	K
Tar					
benzene/ODB/tar	1.00	0.64	0.978	56± 9	0.0096
toluene/1-cloronaphthalene/tar	0.67	0.44	0.981	151 ± 17	0.0032
1-clorobutane/1-cloronaphthalene/tar	1.22	0.99	0.989	77 ± 4	0.0034
38API					
benzene/ODB/38API	0.67	0.55	0.991	24 ± 2	0.0095
toluene/1-cloronaphthalene/38API	1.44	0.31	0.991	94 ± 17	0.0029
1-clorobutane/1-cloronaphthalene/38API	1.63	0.32	0.989	73 ± 4	0.0057
26.5API					
benzene/ODB/26.5API	0.54	0.41	0.990	41 ± 5	0.0075
toluene/1-cloronaphthalene/26.5API	1.70	0.59	0.993	30 ± 3	0.0049
1-clorobutane/1-cloronaphthalene/26.5API	1.94	0.59	0.995	23 ± 6	0.0064

4.6 Conclusion

The dissolution model presented in this study predicted the behavior of the binary pseudo-component chemical systems where real oil mixtures were used. In some cases the real oil was more accurately modeled as contributing to the soluble volume fraction and in others as contributing to the insoluble volume fraction. When benzene was part of the mixture, its high solubility was the major contributor to mass transfer. Conducting experiments using highly soluble benzene and low soluble toluene and 1-clorobutane with crude oils of unknown solubility yielded a range of dissolution constants, K_s [1/s], which could be applied to real oil spills. A time frame can be established with these K_s values for an oil spill of known or estimated soluble volume fraction. However, further experiments with freshly drilled crude oil with both volatile and soluble components would highlight the capabilities and limitations of this model.

CONCLUSIONS

The weathering of chemical-amended crude oils was simulated in the laboratory to study the processes by which negatively buoyant droplets may sink to the bottom of the sea bed from spills on the surface and at depth. Experiments with two crude oils and a tar, as components of the mixtures, were performed so as to more realistically represent oils spilled on water.

Previous studies were done using “oil-like” mixtures made of pure chemicals. These “model-oil” mixtures were used in both evaporative and dissolution weathering experiments. Based on these model-oil studies, the mechanisms that produced sinking oil droplets were observed, numerous data sets were collected, and a theoretical mathematical model was applied. The resulting model concept assumes an oil mixture can be divided into two pseudo-component fractions. Based on the physicochemical properties of the hydrocarbons in natural mineral oils, these complex mixtures can be divide nicely into a volatile/soluble volume fraction (A) and a non-volatile/insoluble fraction (B). The so-called “binary model” was developed and used successfully with the model-oil experimental results. Having a single adjustable parameter, one for evaporation and another for dissolution, the binary model captured the qualitative behavior aspects of the oil sinking process due to weathering. The object of this study was to test the performance of the binary model under laboratory experimental weathering conditions using crude oils and tar.

In the present study nearly identical weathering experiments were done using crude oils and a tar as 10% to 42% of the volume of the spilled-material. In all cases, the observed qualitative behavior patterns of the evapo/sinking and the solute/sinking processes, were identical. In comparing the numerical magnitude of the individual weathering process kinetic parameters, the resulting values with crude oil amended model-oils vs. the pure component model-oils were very similar, statistically. The numerical range of the weathering time-periods, both evaporation and dissolution, for producing negatively buoyant droplets were similar as well. Similar and often time identical measured thermodynamic and kinetic parameters resulted from laboratory experiments for the evaporation and dissolution weathering processes designed to simulate surface and sub-surface spills. Based on these outcomes it appears that the crude oils and tar perform both chemically and physically just as the model-chemicals. The theoretical binary component model was simultaneously verified by the overall investigation. It is a mathematically simple, mass balance derived construction which contains the essential mechanistic features so as to correctly mimic the transport and thermodynamics across both the oil-atmosphere and oil-water interfaces, a necessity for real world oil spills.

Apparently, the oil-like materials used in the present experiments contained very small quantities of the soluble and volatile light constituents normally found in mineral oils. Being so, they were placed in the insoluble/non-volatile B-category of the binary model. This placement in the binary model resulted in a more consistent range of kinetic parameters than being placed in the soluble A-category for evaporation weathering. However, additional testing using natural mineral oils containing significant soluble and volatile components is needed.

The binary pseudo-component approximation both as a concept and in practical application remains problematic at this time. It worked fairly well in this study because the oils were selected and the chemicals used were known to have the correct physicochemical properties; it was clear at the start to which pseudo-component group they belong. In the case of natural mineral oils there is no laboratory testing procedure to use for assigning and quantifying the volatile/soluble and non-volatile/insoluble fractions. In addition the algorithmic procedure of combining individual chemical species from a complex mixture to produce a characteristic and representative vapor pressure or solubility assigned to the binary component, is lacking. In addition the assignment must be consistent with component density assignment so as to realistically capture oil-in-water buoyancy behavior. Although there is a clear need for such models in the field of oil spills, much proof-of-concept work remains to be done so as to hone the accuracy of their predictions.

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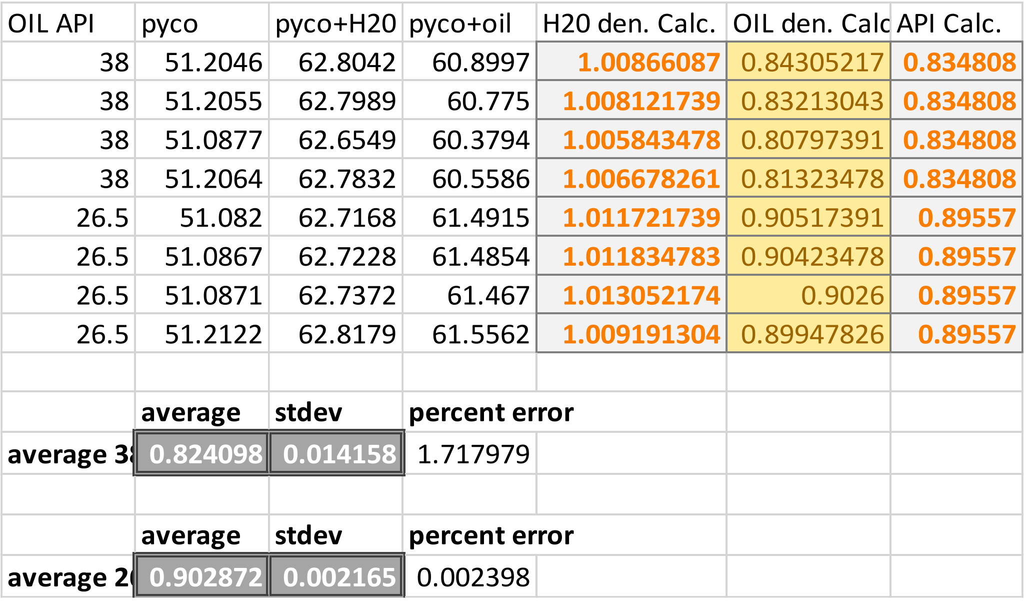
APPENDIX A

Density measurements of 38 and 26.5 API Oil and Tar

11.5mL Pycnometer methods:

1. The empty pycnometer is weighed
2. The pycnometer is filled with water and weighed.
3. The pycnometer is emptied and filled with oil and weighed
4. Subtract the result of step 1 from step 3 and divide by 11.5mL
5. Repeat steps 1-4 for various oils

Density data:



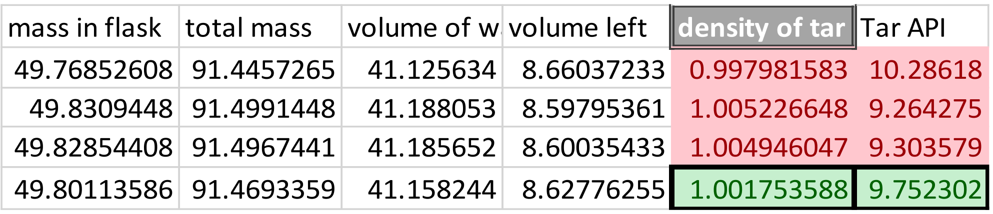
OIL API	pyco	pyco+H20	pyco+oil	H20 den. Calc.	OIL den. Calc	API Calc.
38	51.2046	62.8042	60.8997	1.00866087	0.84305217	0.834808
38	51.2055	62.7989	60.775	1.008121739	0.83213043	0.834808
38	51.0877	62.6549	60.3794	1.005843478	0.80797391	0.834808
38	51.2064	62.7832	60.5586	1.006678261	0.81323478	0.834808
26.5	51.082	62.7168	61.4915	1.011721739	0.90517391	0.89557
26.5	51.0867	62.7228	61.4854	1.011834783	0.90423478	0.89557
26.5	51.0871	62.7372	61.467	1.013052174	0.9026	0.89557
26.5	51.2122	62.8179	61.5562	1.009191304	0.89947826	0.89557
	average	**stdev**	**percent error**			
average 3	**0.824098**	**0.014158**	1.717979			
	average	**stdev**	**percent error**			
average 2	**0.902872**	**0.002165**	0.002398			

Displacement method: TAR

1. Clean and dry (in oven) a 50mL volumetric flask and weigh
2. Fill flask with 30mL of deionized water and weigh
3. Inject ~10mL of tar with a syringe and large bore needle and weigh

4. Fill volumetric flask to level with deionized water.
    a. (Calculations assume density of deionized water is 1 g/mL.
5. Divide mass of tar (measured) by the volume of tar injected (calculated)

Density data: TAR (Bolded and green highlighted values chosen after excess water was cleared away from neck of flask.)



mass in flask	total mass	volume of w	volume left	density of tar	Tar API
49.76852608	91.4457265	41.125634	8.66037233	0.997981583	10.28618
49.8309448	91.4991448	41.188053	8.59795361	1.005226648	9.264275
49.82854408	91.4967441	41.185652	8.60035433	1.004946047	9.303579
49.80113586	91.4693359	41.158244	8.62776255	**1.001753588**	**9.752302**

APPENDIX B

Evapo-Sink Model

The Evapo-Sink model is model consisting of a binary mixture of Component A and Component B. Component A consists of volatile chemicals with a density $\rho_A{}^*$[g/m^3] less than the density of water ρ_w; and Component B consists of non-volatile chemicals with a density $\rho_B{}^*$[g/m^3] greater than water. Pure component molar densities are defined ideally as C_A [mol/m^3]= $\rho_A/M.W_A$ and C_B [mol/m^3]= $\rho_B/M.W_B$ for components A and B. Initial components are combined volumetrically and ideally to yield an initial total volume, $V_o=V_{Ao}+V_B$, of a “spill”. The mass and volume of component A decrease with respect to time; however, the mass and volume of B remain constant. The state variable X(t) is defined as the ratio of the volumes of components A and B with respect to time: $X(t)=V_A(t)/V_B$. This ratio decreases with time as the light volatile component A chemicals evaporate off the surface slick in the air. In laboratory settings the slick thickness h [m] changes with respect to time though the surface area of the slick is modeled as remaining constant. A surface slick may lose component A through mass transport by either evaporation into the air or dissolution in water below. The evaporative flux, N_{AE} [g/s$*$m^2], and the dissolution flux, N_{AS} [g/s$*$m^3], of A are quantified by their respective mass transport rate equations, $N_{AE}(t) = K_A (\rho^*_{AAir} - \rho_{AAir}(t)$ and $N_{AS}(t) = K_w (\rho^*_{Aw} - \rho_{Aw}(t))$. K_A and K_w are the overall air-side and overall water-side MTCs. ρ^*_{AAir} [g/m^3] is the concentration of A in air in equilibrium with A in the oil, $\rho_{AAir}(t)$ is the concentration of A in the atmosphere, ρ^*_{Aw} is the concentration of A in water in equilibrium with A in the oil, and $\rho_{Aw}(t)$ is the concentration of A in the water under the slick. The loss of component A by evaporation and dissolution is equal to the mass rate of change of A within the slick volume which is equal to the surface area times the slick height yielding: $-Sk_A[\rho^*_{AAir} - \rho_{AAir}(t)] - Sk_w [\rho^*_{Aw} - \rho_{Aw}(t)] =$

d[Sh(t)ρ_A(t)]/dt. The background concentration of A in the air and water is considered to be negligible, the MTCs constant, and the limits of integration as being X(t) = X_0 at t=0 to X(t) = X. This integration yields equations 3 and 4 in this work (Stevens,2014).

APPENDIX C

Slick Thickness

Since the oil slicks did not cover the entire surface of the 30L jar used in the Evap-Sink experiments, slick thickness could not be carried out by direct measurement. A procedure was implimented to calculate the slick thickness from photographs of the slicks themselves.

23% benzene, 30% ODB, 47%38API oil mixture at initial conditions X(t=0) forming a slick on a fresh water surface

1. Photograph the slick at initial conditions X(t=0) at a known volume 50mL being sure to capture the total surface.
2. Measure the surface area of the total surface. For this cylindrical jar, Area=πr^2 (r=6.125 inches). Area=128.6 in^2.
3. Print the photograph and cut out the total area of the surface then weigh the paper.
4. Cut out the oil slick portion of the photograph and weigh the paper.
5. The percent area of the slick is the result of step 4 divided by step 3.
6. Use $h_o=\frac{Total\ volume}{area\ of\ slick}$ to find the slick thickness adjusting for units when necessary

Slick Thickness results:

composition	area %	ho [mm]
.5hex+.3ODB+.2tar	0.498798	1.318307
.7B+.2ODB+.1tar	0.533192	1.233267
.55cyclo+.3ODB+.15tar	0.739357	0.889379
.23B+.3ODB+.47API(38)	0.560606	1.172961
.4hex+.3ODB+.3API(38)	0.597464	1.1006
.4cyclohex+.3ODB+.3API(38)	0.843736	0.779353
.4B+.4ODB+.2API(26.5)	0.73848	0.890435
.4hex+.3ODB+.3API(26.5)	0.941582	0.698366
.4cyclohex+.3ODB+.3API(26.5)	0.825741	0.796337

APPENDIX D

Dissolution Model

"A model oil droplet consists of two components, soluble component A and insoluble component B. Mixtures are assumed to form ideal solutions with additive properties, such that V_A and V_B give total volume, V_0. The pure component density of A, ρ_A*, is less than the receiving water and is assumed to be constant for the pressure and temperature range. Solubilization commences upon placement of the oil in water and the mass of A, $M_A(t)$, can be expressed through its volume decrease by $M_A(t) = \rho_A* V_A(t)$ while V_B remains constant so that $M_B = \rho_B* V_{B0}$. As previously defined in the EVAPO-SINK model, the state variable is the volume ratio of the soluble to the insoluble component, $X(t) = V_A(t)/V_{B0}$. The concentration of A in the droplet is given by $\rho_A(t) = (\rho_A* X(t))/(X(t) + 1)$, and for B, $\rho_B(t) = \rho_B*/(X(t) +1)$. As dissolution commences with time, the concentration of A decreases and the density of the drop will approach that of water, ρ_w. As mass is lost from the droplet, the diameter, surface area, and volume of the drop will decrease. For a single sphere, $V(t) = \pi d(t)^3/6$ and $A(t) = \pi d(t)^2$. In terms of the state variable the droplet diameter is $d(t) = [(X(t) +1)/(X_0 + 1)]^{1/3}d_0$. With the initial drop density obtained from $d_0 = (6V_0/\pi)^{1/3}$ with surface area is $A(t) = \pi d_0^2[(X(t) +1)/(X_0 + 1)]^{2/3}$. At this juncture all the time varying parameters are expressed in terms of the state variable. The flux of the soluble fraction during dissolution from the oil-phase to the water-phase, $N_A(t)$ [g/m^{2}s], equals $K_w(\rho^*_{AW} (t) - \rho_{AW})$, where K_w [m/s] is the overall water-side mass transport coefficient, $\rho^*_{AW} (t)$ is the solute concentration in water in equilibrium with the oil and ρ_{AW} is the remote solute concentration in water. For estimates of K_W the two-resistance theory is required. It includes the oil-side transport as well as the water-side transport coefficient.

The linear equilibrium assumption (LEA) is used with an oil-to-water partition coefficient, $K^*_{Oil/W}$, for quantifying the solute equilibrium at the interface and between the bulk phases. As used here it is ρ^*_{AW} (t) ≡ ρ_A(t)/$K^*_{Oil/W}$ = ρ^*_AX(t)/(X(t)+1)$K^*_{Oil/W}$. The mass transfer coefficient, K_w, is assumed constant and correlations are available in the literature for its estimation. $K^*_{Oil/W}$ for the soluble component is also assumed constant. A mass balance on the soluble component is performed and used for developing the binary dissolution model. It is extended to project the dissolution time-period necessary for droplets to achieve negative density. In combination the final product is termed the solute-sinking model or "SOLUTE-SINK". All droplets of same size behave alike. A mass balance on the soluble fraction for an oil droplet of diameter d_0 [m] has the rate of dissolution [g/s] from the droplet equal the mass rate of change of A within: $-A(t)K_W(\rho^*_{AW}(t)- \rho_{AW}) = d(m_A(t))/dt$. Assuming the background soluble concentration in water, $\rho_{AW,}$ is zero and substituting the appropriate state variable relationships developed above for the time-varying terms: $-\pi d_0^2[(X(t)+1)/(X_0+1)]^{2/3} K_W[((\rho_A*)/(K^*_{Oil/W}))((X(t))/(X(t)+1))-0] = d/(dt)[\rho_A^*X(t)V_{BO}]$." (Steven, 2014) This simplifies to equations 9 and 10 in this work.

VITAE

Cameron Loebig graduated from Jesuit High School (New Orleans) in May, 2005. He attended LSU in the fall of 2005 and graduated in 2010 with a bachelor's degree in Chemistry. He then began to work at TJH-2B as a lab tech where he conducted testing for insulating oils for PCBs, dielectric breakdown points, acid content, interfacial tension, as well as other physical properties. He then began working at Albemarle Corporation Process Development Center (PDC) as a reactor technician. This was a research position testing polymeric catalysts developed for polyethylene, polypropylene, and alpha-olefin production. During his time at Albemarle he entered the chemical engineering program for transitioning students at LSU (2011). In 2013, he entered LSU's Graduate program for Chemical Engineering as a full time student, working with Dr. Thibodeaux on modeling deep sea oil spills.