

THE DYNAMICS OF ORIMULSION IN WATER WITH VARYING ENERGY, SALINITY AND TEMPERATURE

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ABSTRACT

Orimulsion is an oil-in-water emulsion of Venezuelan bitumen. Orimulsion was found to behave predictably in salt (33‰ NaCl) and fresh water, driven by buoyancy to rise in salt water and sink in fresh water; but behaviour in brackish water (20‰ NaCl) was difficult to predict. Temperature has also been indicated as having an influence on Orimulsion behaviour. The current study extended experimentation down to lower temperatures, and a variety of mixing energies.

This study resulted in new information on the behaviour of Orimulsion spills in salt, fresh, and brackish water with salinity values of 20 and 33 degrees at temperatures of 5 and 15 degrees Celsius. Energy was varied by adjusting the applied rotational field and measurement with thermal probes. Depletion rates and characteristics were determined by adding Orimulsion to a 300-L tank of water, taking a time series of samples, and determining the concentration of bitumen and the particle size distribution. Changes in bitumen concentration and particle size distribution as a function of time were also measured. Using these data, simple equations were developed to describe and predict the concentration of bitumen in the water column as a function of time. Similarly nomograms showing the amount of oil on the bottom and on the water surface are presented.

INTRODUCTION

Orimulsion is a surfactant-stabilized oil-in-water emulsion of 70% bitumen in 30% water (Bitor, 1996). Its behaviour when spilled is very different from that of conventional fuel oils. The base bitumen has a density of 1.0202 g/mL at 15°C. In absence of circulation in the water column, the droplets of Bitumen will float in seawater with a typical density of 1.022 g/mL, but will slowly sink in waters of less density. In actual fact, the sinking/rising behaviour of the droplets is complex because they are close to neutrally buoyant in any type of water. In freshwater, droplets have a tendency to sink through the water column. In laboratory tests of various scales, the droplets largely collected near the bottom and only about one half would directly deposit on the bottom (Jokuty et al., 1999a, 1999b; Ostrazeki et al., 1997). In full saline water (about 33‰), large portions of the product will rise to the surface and remain there. In all cases, significant quantities of bitumen remain in the water, especially with high sea energy. The purpose of this series of tests was to quantify the dynamics of the Orimulsion particles with varying salinity and temperature.

Previous studies on the dynamics have been conducted (Fingas et al., 2002, 2003). This series of tests have been expanded to

include more precise mixing and more variables in terms of the energy input, temperature and salinity.

EXPERIMENTAL

Summary of Test Method

Orimulsion was added to 300 L of water in a cylindrical tank at mid-depth. At prescribed time intervals, samples were taken from the tank at mid-depth and analyzed for oil content by extraction and subsequently weight. Coalesced bitumen was removed from the top of the water and weighed at the end of the experiment.

Reagents and Equipment

The apparatus consisted of a cylindrical tank 75 cm in diameter and 110 cm in height, and a mixer with two propellers. The Orimulsion-400 used for these experiments was a composite sample obtained from a shipment received at Dalhousie, New Brunswick in September, 2003. A total of 21 experiments were run.

For each test, the tank was filled to a depth of 68 cm, yielding a volume of 300 L of water. Salt was added as appropriate to obtain the desired salinity. Salinity was checked with a Horiba U-10 water quality tester. The temperature of the water was either 15°C or 5°C.

For each run, approximately 400 mL of well-mixed Orimulsion at the test temperature was measured into a graduated cylinder, and weighed. The Orimulsion was added at mid-depth in the tank, using a standard 60 mm diameter glass powder funnel and glass tubing. The bitumen to water ratio was approximately 1:1000. The funnel and tubing were rinsed with 500 mL of tank water. The graduated cylinder was weighed again, and the mass of Orimulsion added was determined by difference. For all runs the Orimulsion was added with the mixer in action, and timing of the run began as soon as Orimulsion was released into the water. Agitation was continued for 48 hours.

At intervals, water samples were withdrawn from the tank for either particle size analysis or bitumen concentration determination. To ensure that samples were always collected from the same depth and location, plastic tubing was secured to a sampling jig suspended from the top of the test tank. Samples were withdrawn using standard 60-mL plastic syringes. Bitumen concentration samples were taken at the middle of the tank. Coalesced bitumen was collected from the top of the tank (near the outer wall) at the same time as the water sample was taken. The bitumen was removed using a piece of sorbent and its amount determined by weight.

At the end of an experiment, the bitumen left on the bottom and walls of the tank was scrapped off using a putty knife.

The bitumen was weighed. The bitumen adhered to the shaft was determined by subtracting the weight of the shaft from the total weight. The weights of all three bitumen depositions were combined.

Table 1 summarizes the conditions for each experiment. Data was obtained for a total of 342 concentration samples and approximately the same particle size samples.

Particle Size

Particle size distribution was determined using a Coulter Counter Multisizer with AccuComp software. The Coulter Counter determines particle size by measuring the change in voltage as a particle passes through a small aperture between two electrodes. The particles are suspended in an electrolytic solution that is drawn by vacuum suction through a small aperture separating two electrodes under applied current. As a particle passes through the aperture, there is an increase in resistance between the electrodes that results in a voltage pulse. The magnitude of the voltage pulse is proportional to the volume of the particle passing through the aperture. The voltage pulses are scaled and counted by the AccuComp software package, which can then mathematically manipulate the data to provide particle size distribution information.

Orimulsion Water Column Concentration

Each water sample was extracted in a 125-mL separatory funnel with three 25-mL portions of dichloromethane. The extracts were collected and combined and dried by passes through a sodium sulphate layer in a funnel. The extracts were concentrated by rotary evaporation in pre-weighed evaporation flasks. The bitumen residue was weighed, and the concentration calculated as g/L of bitumen in water.

RESULTS

Table 1 provides a summary of data collected from the experiments. Detailed data will be published in the future. Table 1 shows the experimental conditions under which the experiment was conducted including salinity, rpm of the mixer, Orimulsion added, and temperature. Three sets of particle sizes were recorded, sizes

Table 1. Summary Data of Experiments Conducted

Experiment number	Temperature °C	Water salinity ‰	Stirring Speed rpm
1	15	0	120
2	15	33	120
3	15	0	240
4	15	33	240
5	15	0	480
6	15	33	480
7	15	20	480
8	15	20	120
9	5	0	240
10	5	20	240
11	5	33	240
12	5	0	120
13	5	20	480
14	5	0	480
15	5	20	120
16	5	33	480
17	5	33	120
18	15	0	0
19	15	20	0
20	15	20	240
21	15	33	0

at the VMD or Volume Mean Diameter sizes above 10 µm and sizes above 20 µm. This division is necessary as salt clusters have sizes ranging from about 1 to 12 µm. The bitumen particles largely appear above 10 µm. So there is an overlap between measuring the bitumen sizes and interference from the salt water. The 20 µm and greater set, which will be largely used here, contains little salt interference, but may miss some smaller bitumen droplets. As time moves on, most of these smaller (< 20 µm) particles have coalesced to form larger particles. As larger particles are removed by coalescence or adhesion to sides, bottom or the shaft, there is an apparent shift in particle size to smaller values which is due to a greater contribution from background non-bituminous particles such as salt. The surfactant-stabilized Orimulsion has volume mean diameter of 20 µm. Once in the water, the surfactant rapidly leaches out and droplets can coalesce. This occurs rather rapidly. In fact, droplets rapidly coalesce past 70 µm VMD, however some particles will remain in the water column with 20 to 50 µm VMD sizes. Salinity appears to affect coalescence rate significantly.

The amount of bitumen recovered from the bottom, sides or impeller was recorded if this was significant. This amount of bitumen is particularly large in the case of the freshwater situation.

DEVELOPMENT OF PREDICTOR EQUATIONS

The values of concentrations appear to be regular and thus could lead to a more universal set of equations. With this end in mind, the data, as summarized in Table 1, the amount left on the surface, the energy, salinity and temperature were curve fit using the program TableCurve 3d. Because there are more than one independent variables, including temperature, time, and salinity, TableCurve was used to generate the form of the best equation. This resulted in best fits with 2 independent variables, but yielded information on the best mathematical parameters. Then these were used in the program DataFit from Oakdale Engineering to create final equations. DataFit from Oakdale engineering can yield linear solutions on many independent variables.

This resulted in the following equations.

Amount on Top

$$\text{Percent on top} = \exp [.04\sqrt{\text{time}(\text{min})} + 3.5\sqrt{\text{salinity}} - 0.10\ln(\text{energy}) + 0.03\text{Temp C} - 17.9] \quad (1)$$

Concentration in the Water column

$$\text{Percent in water} = -11.5\ln(\text{time}(\text{min})) - 1.3(1/\text{salinity}) - 11(1/\text{energy}) + 15(1/\text{Temp C}) + 150 \quad (2)$$

Particle Size (>20 µ)

$$\text{size } (\mu\text{m}) = -0.09\sqrt{\text{time}(\text{min})} - 110*[\ln(\text{salinity})]/\text{salinity} + 0.19\text{Temp C} + 28 \quad (3)$$

Particle Size (Direct VMD)

$$\text{size } (\mu\text{m}) = -0.17\sqrt{\text{time}(\text{min})} - 138*[\ln(\text{salinity})]/\text{salinity} + 0.26\text{Temp C} + 11 \quad (4)$$

Particle Size (>10 µ)

$$\text{size } (\mu\text{m}) = -0.15\sqrt{\text{time}(\text{min})} 128*[\ln(\text{salinity})]/\text{salinity} + 0.2\text{Temp C} + 18.5 \quad (5)$$

A few considerations must be noted for these calculations. The statistics on these are given in Table 2. The regression coefficient, r^2 , is a measure of the overall model correlation fit. An r^2 of 1 is a perfect model, values of r^2 below about 0.6 indicate a poor model. The standard error is the standard deviation of the regression parameter in question. The larger this parameter is, the more it is prone to error in predicting the value in question. The t-ratio is the ratio of the parameter value to its standard deviation. The larger the t-ratio, the more significant this parameter is to the regression. Prob(t) is the probability associated with the t-test. This value gives the importance of the particular variable in the

Table 2 Statistical Results on Prediction Equations

Model for Predicting Amount (%) Remaining on Surface

$Y = \exp(a*x1+b*x2+c*x3+d*x4+e) \quad r^2= 0.94$

Variable	Value	Standard Error	t-ratio	Prob(t)
a Time (square root)	0.04	0.002	24.8	0.0
b Salinity (square root)	3.47	1.43	2.43	0.02
c Energy (log)	-0.10	0.02	-5.17	0.0
d Temperature	0.03	0.004	7.29	0.0
e constant	-17.9	8.22	-2.18	0.032

Model for Predicting Amount in the Water Column

$Y = a*x1+b*x2+c*x3+d*x4+e \quad r^2= 0.75$

Variable	Value	Standard Error	t-ratio	Prob(t)
a Time (ln)	-11.5	0.631	-18.2	0.0
b Salinity (1/x)	-1.34	0.34	-3.99	0.00011
c Energy (1/x)	-10.9	4.23	-2.58	0.011
d Temperature (1/x)	14.7	20.2	0.73	0.47
e constant	150	4.96	30.1	0.0

Model for Predicting Particle Size—Direct VMD

$Y = a*x1+b*x2+c*x3+d \quad r^2= 0.95$

Variable	Value	Standard Error	t-ratio	Prob(t)
a Time (square root)	-0.17	0.0237	-7.3	0.0
b Salinity (lyx/x)	138.0	6.1	22.5	0.0
d Temperature	0.26	0.10	2.7	0.01
e constant	10.98	1.59	6.9	0.0

Model for Predicting Particle Size—>10 µ VMD

$Y = a*x1+b*x2+c*x3+d \quad r^2= 0.94$

Variable	Value	Standard Error	t-ratio	Prob(t)
a Time (square root)	-0.15	0.0257	-5.8	0.0
b Salinity (lyx/x)	128	6.7	19.1	0.0
d Temperature	0.20	0.10	1.9	0.07
e constant	18.5	1.73	10.7	0.0

Model for Predicting Particle Size—>20 µ VMD

$Y = a*x1+b*x2+c*x3+d \quad r^2= 0.88$

Variable	Value	Standard Error	t-ratio	Prob(t)
a Time (square root)	-0.09	0.03	-3.2	0.00
b Salinity (lyx/x)	110	7.4	15.0	0.0
d Temperature	0.19	0.12	1.6	0.12
e constant	28	1.92	14.5	0.0

model at hand. The higher the value of the Prob(t), the greater the probability that the variable could be eliminated from the model with minimal loss to its prediction capability.

The energy was calculated using a simple mechanical method and measured using a thermal probe. These methods are detailed in another paper (Fingas, 2004). The energy was input into the equation based on the rpm of the mixing. Table 3 shows the estimated correspondence in energy to sea state as calculated from the Fingas (2004) reference.

Table 3 Energy Input Values for the Model

(Values calculated from Fingas, 2004)

Input to Orimulsion Model	Approximate Wave Height (m)	Wind Speed (m.s)	rpm
2	0.5	5	60
4	1	10	120
16	2	20	240
64	3	30	480
128	4	40	960

It should be noted that energy is not in the particle-size prediction equations. It was found that it was not needed and in fact, lowered the quality (by statistics) of the fit of the model. Energy is more important for prediction of amount remaining on the surface as compared to particle size and even oil remaining in the water column. An examination of the t-ratio of the various parameters (Table 2) shows the importance of the various factors.

Based on a simple assumption of mass balance for bitumen in a test tank, the amount of the bottom can be calculated from the amount in the tank less the amount of the top yields the amount on the bottom.

A graph for the amounts on the top was calculated using the equation (1), Figure 1. The graph for the calculated amount of bitumen remaining in the water column is shown in Figure 2. Figure 3 shows a graph of the predicted amount of bitumen on the bottom with time. This nomogram is calculated simply as a mass balance. Figure 4 shows calculated particle size with time, temperature and salinity.

CONCLUSIONS

Studies have shown that Orimulsion is driven by buoyancy to rise in salt water and sink in fresh water. The current study extended experimentation to include energy as a factor and included the previous factors of temperature and salinity. This study shows that there is a complex interaction among salinity, time, energy and temperature. The interaction between these was measured in 21 experiments and data used to provide a correlation between the data and predictors for the bitumen rising to the surface and

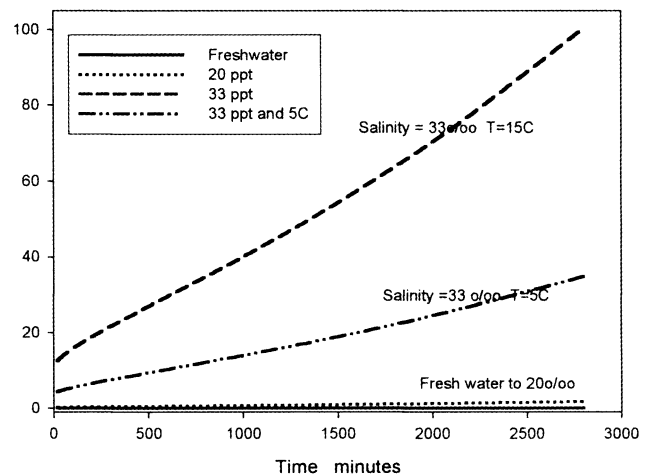


FIGURE 1 ILLUSTRATION OF THE BITUMEN APPEARING ON THE SURFACE AS A FUNCTION OF SALINITY

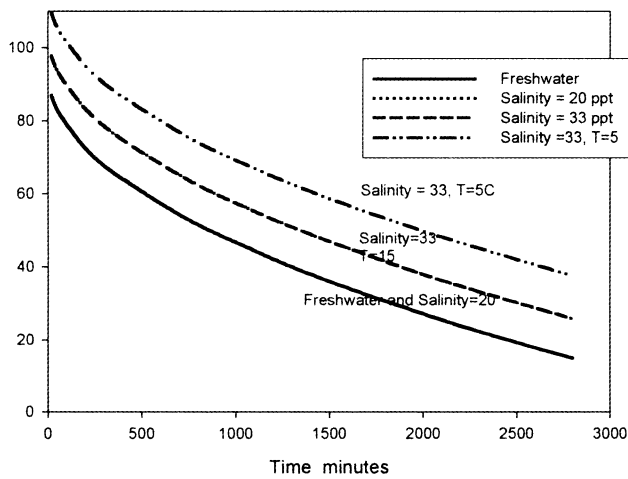


FIGURE 2 BITUMEN IN THE WATER COLUMN AS A FUNCTION OF SALINITY AND TIME

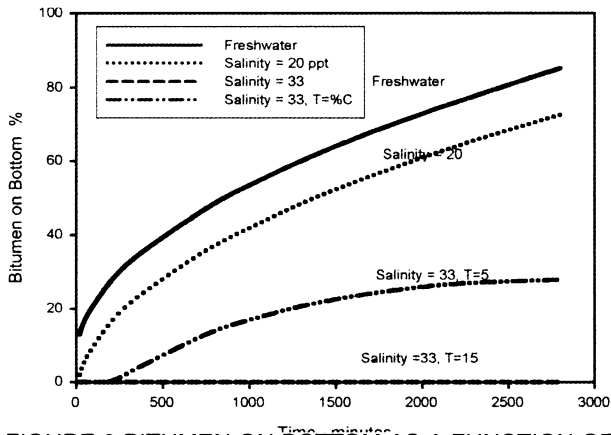


FIGURE 3 BITUMEN ON BOTTOM AS A FUNCTION OF TIME AND SALINITY

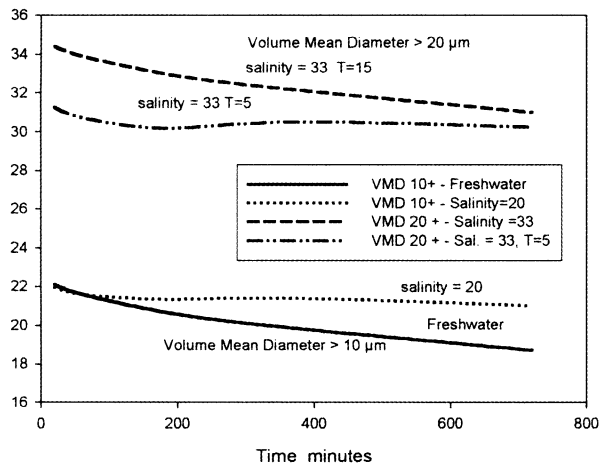


FIGURE 4 VMD PARTICLE SIZE OF DROPLETS IN WATER WITH TIME, SALINITY AND TEMPERATURE

bitumen concentration in the water column. Measurement of bitumen rising to the surface was conducted at each measurement interval, thus this data

Changes in bitumen concentration, amount on the surface and particle size distribution as a function of time were measured. Using these data, simple equations were developed to describe and predict the concentration of bitumen in the water column as a function of time. Similarly graphs are presented showing the amount of oil on the bottom and on the water surface with time

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BIOGRAPHY

Merv Fingas is Chief of the Emergencies Science and Technology Division in Environment Canada. Dr. Fingas’ speciality is research in the analysis and behaviour of oil spills in the environment. He manages 15 other scientists and staff studying various aspects of oil and chemical spills. He has devoted the last 30 years of his life to spill research and has over 600 papers and publications in the field.

REFERENCES

Bitor America Corporation, 1996. *Summary of Studies Conducted on the Environmental Fate and Effects of Orimulsion*, Version 1.0, Bitor America Corporation, Boca Raton, Florida, 46 p.

Fingas, M.F., Z. Wang, P. Jokuty, M. Landriault, and J. Noonan, 2002. “Studies on the Behaviour of Orimulsion in Freshwater and Seawater”, in *Proceedings of the Third R&D Forum on High-density Oil Spill Response*, International Maritime Organization, London, UK, pp. 421-425.

Fingas, M.F., Z. Wang, M. Landriault, J. Noonan, and R. MacKay, 2003. “The Effect of Varying Salinity and Temperature on the Dynamics of Orimulsion in Water”, in *Proceedings of The 2003 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 419-427.

Fingas, M.F., 2004. “Measurement of Energy in Laboratory Vessels”, in *Proceedings of the Twenty-Seventh Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 1-18.

Jokuty, P., S. Whiticar, Z. Wang, K. Doe, B. Fieldhouse, and M.F. Fingas, 1999a. *Orimulsion-400: A Comparative Study*, Environment Canada Manuscript Report EE-160, Ottawa, Ontario, 26 p.

Jokuty, P., B. Fieldhouse, S. Whiticar, and M.F. Fingas, 1996b. *The Dynamics of Orimulsion Spills in Salt, Fresh, and Brackish Water*, Environment Canada Manuscript Report EE-161, Ottawa, Ontario, 37 p.

Ostazeski, S.A., S.C. Macomber, L.G. Roberts, A.D. Uhler, K.R. Bitting and R. Hiltabrand, 1997. “The Environmental Behaviour of Orimulsion Spilled on Water”, in *Proceedings of the 1997 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp 469-477.