

Spreading and Retraction of Spilled Crude Oil on Seawater

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ABSTRACT 300207:

Oil-spills due to release of crude oil from tankers, offshore platforms, drilling rigs, and wells, and of other products such as diesel and bunker fuel, if uncontrolled, may have serious and sometimes long term environmental impact. This paper presents a method for reducing the areal coverage of spilled oil at sea or over other aqueous surfaces. The method can be used to contain spilled oil more efficiently during or after placement of booms.

The surface tension of seawater causes rapid spreading of spilled oil over large distances. However, spreading of oil can be instantly reversed by reducing the surface tension of the seawater by means of minimal quantities of surfactant. A low concentration of a water-soluble surfactant, such as a non-ionic surfactant with low critical micelle concentration, is recommended for maximum effectiveness for the least amount of surfactant. A controlled amount of the surfactant may be continuously deployed at the inner-wall of the boom. The spilled oil is caused to retract away from the boom toward the center of the encircled area. The decrease in area of the spilled oil results in a thicker oil layer that can be removed more effectively by skimming. The deployed surfactant also reduces the amount of oil that adheres to the control boom. The boom can then easily be removed from a remediated oil-spill and reused at a later date with minimal cleaning.

Laboratory observations show how crude oil can migrate over the surface of a model oil-wetted boom. Modification of the spreading behavior of five different crude oils by a non-ionic surfactant, BIO-SOFT®, was investigated. Experiments on spreading and contraction confirmed predictions based on interfacial tension measurements for seawater/air, crude oil/water and crude oil/air before and after release of a very small amount of surfactant. The retraction of crude oil as a function of surfactant concentration is demonstrated by real time video recordings of laboratory experiments.

INTRODUCTION:

Oil spills may be controlled by chemical dispersion, combustion, mechanical containment, and/or adsorption. Controlled burning can reduce the amount of oil on water, but can only be done in low wind conditions. Dispersants create smaller oil droplets which may be scattered by currents followed by biodegradation. Dry hydrophobic, water insoluble polymers that both adsorb and absorb hydrocarbons can clean up oil spills by changing the physical state of oil from liquid to a semi-solid or a rubber-like material that floats on water, rendering it readily collectable. However, the material must then be disposed of in landfills, recycled as an additive in asphalt or rubber products, or burned as a low ash fuel. Oil-absorbing/adsorbing materials may also be used. Oil may be “vacuumed” from the surface, along with some water,

and the mixture centrifuged to separate the oil from the water, which is usually returned to the sea. Oil skimming devices may also be used. Typically, large floating barriers, known as booms, are used to surround and contain oil slicks.

The spreading of oil on a water surface can be described by:

$$S = \gamma_{w/a} - (\gamma_{o/a} + \gamma_{w/o}) \quad (1)$$

where S is the spreading coefficient, and $\gamma_{w/a}$, $\gamma_{o/a}$, and $\gamma_{w/o}$ are the surface tension of water, the surface tension of oil, and the interfacial tension between oil and water, respectively. The surface tension of seawater, $\gamma_{w/a}$, is about 74 mN/m. For typical crude oils, the surface tensions of oil against air, $\gamma_{o/a}$, are between 20 mN/m and 30 mN/m and the interfacial tensions, $\gamma_{w/o}$, are between 15 mN/m and 30 mN/m. Oil spreads spontaneously when $S > 0$. The combination of low surface and interfacial tensions of crude oil, and the high surface tensions for seawater result in a high, positive spreading coefficient, $10 < S < 30$ mN/m. Consequently, after an oil spill, crude oil spreads rapidly over water. This can be an advantage in the application of dispersants to thin oil films (Nedwed and Coolbaugh, 2008). However, if the objective is to recover the oil from the spill site, often for environmental reasons, oil spreading needs to be avoided.

Water-insoluble monomolecular films can be used to compress spilled oil into lenses of increased thickness that occupy smaller surface area, and allow easier mechanical retrieval (Garrett and Barger, 1970). Another approach to reversal of the spreading of an oil slick is by reducing the surface tension of the water with minimal amounts of water soluble surfactants (Takamura et al., 2013). A controlled amount surfactant, for example, a very low concentration of non-ionic surfactant, may be continuously discharged at the inner wall of an oil-spill control boom surrounding the oil spill. The spilled oil is caused to retract away from the boom such that the oil layer becomes thicker and can be removed more effectively. The surfactant also reduces the amount of oil that adheres to the surface of the spill-control boom. The boom can then be removed from a remediated oil spill and reused at a later date with minimal or even without further cleaning.

EXPERIMENTAL:

A non-ionic surfactant, BIO-SOFT® N91-8 (Stepan, Illinois, USA) was used as received. The surfactant is characterized as $\text{CH}_3(\text{CH}_2)_n\text{O}(\text{CH}_2\text{CH}_2\text{O})_y\text{H}$, where $n=8-10$ and the average moles of ethoxylation, $y=8.3$. The composition of a synthetic seawater is given in Table 1. The surface tension of the seawater (34,690 ppm) at pH=6-7 was measured as a function of concentration of BIO-SOFT® N91-8 (Stepan, Illinois, USA) using the Wilhelmy plate method as adapted for the Krüss K100 tensiometer. A Krüss DVT-10 drop volume tensiometer was used to measure the interfacial tension between crude oil and seawater.

Table 1. Composition of Synthetic Seawater and Its Density

Composition	g/L
NaCl	28.0
CaCl ₂ .2H ₂ O	1.6
MgCl ₂ .6H ₂ O	11.6
KCl	0.9
NaN ₃	0.2
TDS	35.5 (34,690 ppm)
Density = 1.024 g/cm ³	

For most of the spreading experiments, approximately 35 mL of the synthetic seawater was placed in a glass beaker of 5.5 cm inside diameter and 3.5 cm height. A drop of the crude oil (~50 μ L) was then placed on the water surface from a disposable glass pipette and spreading behaviour was video recorded.

RESULTS:

Spreading of crude oil on seawater

Five crude oils of widely different properties were selected to examine their spreading behaviour on synthetic seawater at room temperature. Some physico-chemical properties of these crude oils at 20°C are listed in Table 2 together with the calculated spreading coefficient (S) from Equation (1) using their surface and interfacial tensions and $\gamma_{w/a}=73.5$ mN/m. Detailed discussion of spreading behaviour can be found in Takamura et al. (2012). Additional properties of these crude oils can be found in Buckley and Fan (2007) and Loahardjo (2009).

Table 2. Selected physico-chemical properties of five crude oils used for investigation of spreading on seawater. All measurements are at 20°C.

Crude Oil	Aromatics %	Asphaltenes (n-C ₆) %	Resins %	Density g/cm ³	Surf. Ten. mN/m	Int. Ten. ¹ mN/m	S mN/m	Visc. mPa s
Lustre	18	1.0	9.0	0.840	25.2	20.5	27.8	5.0
Gulfaks	26	0.3	16	0.894	28.1	18.4	27.0	35
Cottonwood	23	2.9	17	0.893	27.3	21.6	24.5	26
LC	25	3.2	12	0.903	28.0	25.7	19.8	39
Minnelusa	20	9.1	13	0.904	28.8	27.4	17.2	58

¹against seawater at pH=6-7

Spreading behaviour of three crude oils; a) Gulfaks, b) Cottonwood, and c) LC are summarized in Figure 1 as a series of photographs illustrating the initial spreading of the crude

oil on seawater. Calculated spreading coefficients for these crude oils are much higher than for pure alkanes and aromatics of similar γ_0 ($S < 10$ mN/m), and range from 17 to 28 mN/m, as shown in Table 2. All of the tested crude oils spread rapidly to form a thin layer on the surface of the seawater. The layer thins continuously as long as the spreading coefficient remains positive. The relationship between the thickness of the spreading oil as a function of S and density was formulated by Langmuir (1933). Cochran and Scott (1971) developed an equation which related the spreading rate of the thin oil layer over the surface of water to the combined effect of the spreading pressure, gravitational forces, and hydrodynamic resistance which is a function of the crude oil viscosity.

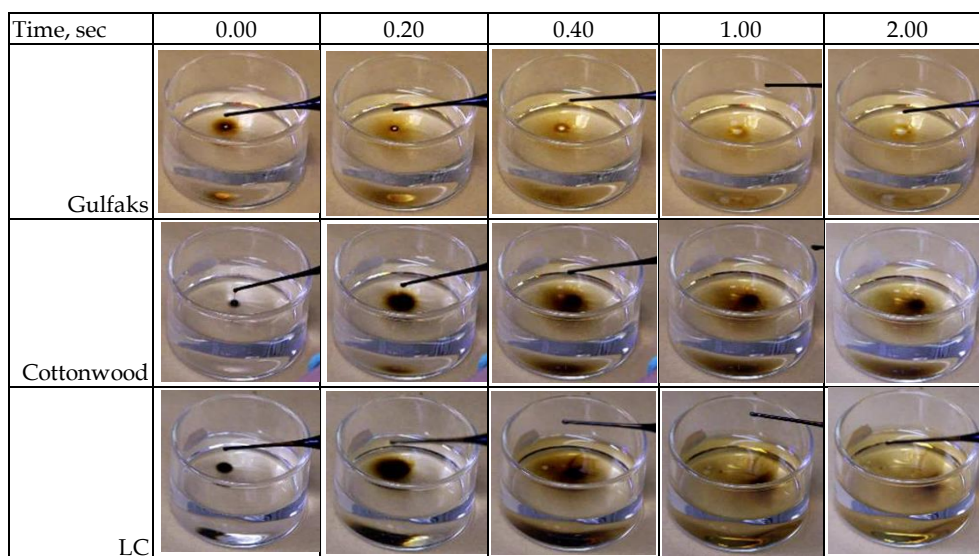


Figure 1. Spreading behaviour of a drop ($\sim 50\mu\text{L}$) of selected crude oils on seawater at 20°C .

Control of the spreading of crude oil on seawater

Even very low levels of surfactant concentration, especially a non-ionic, are known to effectively lower the surface tension of water. Addition of as little as 30 ppm BIO-SOFT® N91-8 lowered $\gamma_{w/a}$ of the seawater by 28 mN/m from 73 to 45 mN/m (see Figure 2(a)). The diagonal line shows typical surface tension behavior as a function of surfactant concentration. In the region between small added amounts up to about 300 ppm, the surfactant accumulates at the water surface, thereby reducing the surface tension. At a certain concentration, termed the critical micelle concentration (CMC), which is specific to each surfactant (approximately 300 ppm for BIO-SOFT), the surface is saturated with surfactant molecules and there is no further decrease in surface tension with increase in surfactant concentration. Above the CMC, the added surfactant molecules form micelles in the water phase.

Figure 2(b) presents the measured interfacial tensions of 5 crude oils as a function of the concentration of the same non-ionic surfactant. The $\gamma_{w/o}$ of the crude oil/seawater interface is already low, even in the absence of this non-ionic surfactant. The $\gamma_{w/o}$ of Minnelusa oil is reduced by only 8 mN/m, from 27 to 19 mN/m, with 30 ppm BIO-SOFT® N91-8. Detailed discussion of the interfacial tension and the micellar structure of the surfactant molecules at the oil/water interface can be found in Hoffmann (1990). The addition of surfactant should decrease

the seawater surface tension more than it decreases the oil/water interfacial tension; therefore, the reduced spreading behavior (quantified as the spreading coefficient) causes the oil slick to retract and form oil lenses.

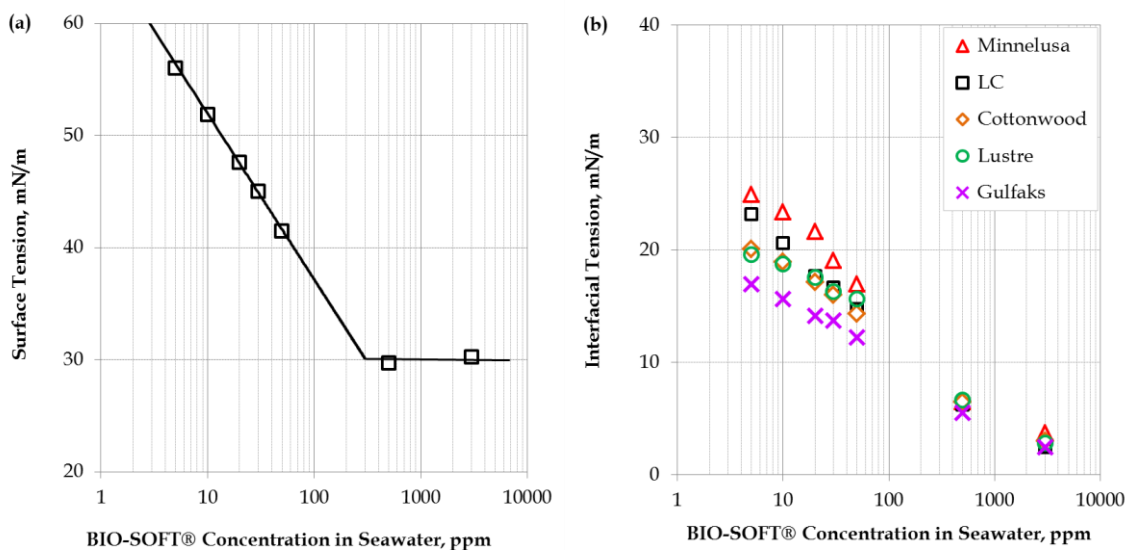


Figure 2. The surface tension of the seawater (a) and interfacial tension of 5 crude oils (b) as a function of the non-ionic surfactant, BIO-SOFT® N91-8, concentration

From Equation (1), it is predicted that addition of even a small amount of non-ionic surfactant to the water would prevent spreading of crude oil ($S < 0$) over the surface of seawater. The spreading coefficients for five crude oils, calculated as a function of BIO-SOFT® N91-8 concentration, are given in Table 3. The S values in the table were calculated using the measured $\gamma_{w/o}$ of each crude oil against seawater and for seawater with a given concentration of BIO-SOFT® N91-8.

Table 3. Calculated spreading coefficients (S) and observed spreading behaviour of five crude oils on seawater. INT (intermediate) indicates that slow spreading of the oil droplet was observed.

Crude oil	Calculated spreading coefficient					Crude oil	Initial Spreading Behavior				
	Seawater with BIO-SOFT®, ppm						Seawater with BIO-SOFT®, ppm				
	0	5	10	20	30		0	5	10	20	30
Lustre	28	10	6	2	-1	Lustre	SP	INT	INT	NO	NO
Gulfaks	27	10	5	1	-1	Gulfaks	SP	INT	INT	NO	NO
Cottonwood	25	7	3	-1	-4	Cottonwood	SP	INT	INT	NO	NO
LC	20	2	-2	-6	-9	LC	SP	NO	NO	NO	NO
Minnelusa	17	0	-4	-9	-11	Minnelusa	SP	INT	INT	NO	NO

The spreading behaviour of Minnelusa crude oil over seawater, shown in Figure 3, clearly demonstrates that as little as 5 ppm (~1.6% of the critical micelle concentration) of the non-ionic surfactant is enough to prevent the rapid spreading of the crude oil.

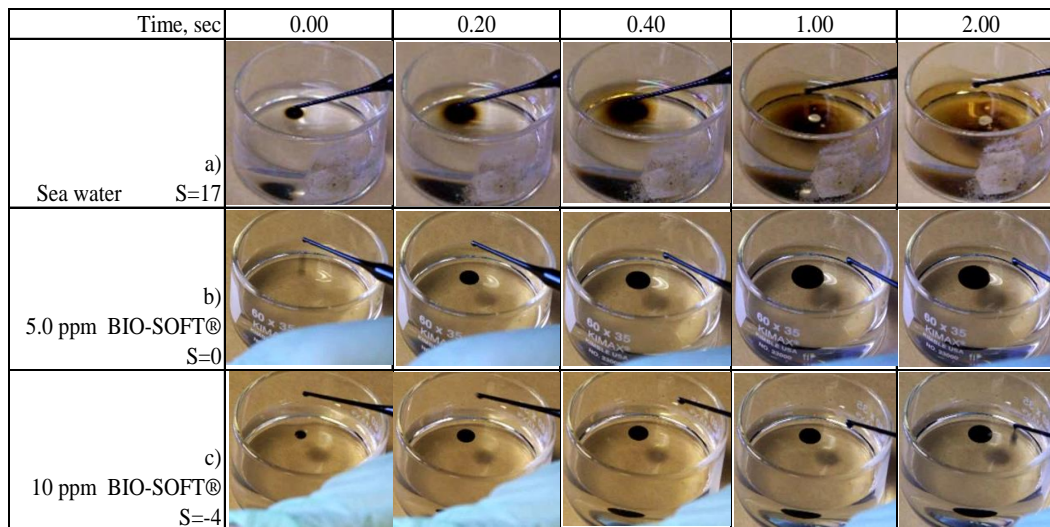


Figure 3. Spreading behaviour of Minnelusa crude oil on seawater in a) the absence and b) the presence of 5 and c) 10 ppm BIO-SOFT® N91-8

Retraction of spilled crude oil

Results shown in Figure 3 and Table 3 show how placement of a small amount of the aqueous non-ionic surfactant solution can effectively cause retraction of the spilled crude oil on the water surface. This is demonstrated in Figure 4a, where a drop of Minnelusa crude oil ($S=17$ mN/m) spread very quickly over the seawater surface (nominal time=0 sec). The thin film of crude oil quickly retracts to form a lens after a drop of 500 ppm aqueous BIO-SOFT® N91-8 solution was added near the side wall of the glass beaker. The retraction of a thin film of crude oil was observed for all five crude oils tested in this study. Thus, application of a small amount of surfactant solution (far less than required for the surfactant to act as a dispersant) can cause the oil to form a thick lens.

For oil contained within booms or some other mechanical barrier, the amount of surfactant required for sufficient lowering of the surface tension is small and can be readily replaced from a local source. The spilled crude oil is then more manageable and can be either skimmed mechanically from the open water surface or burned (Cochran and Scott, 1971).

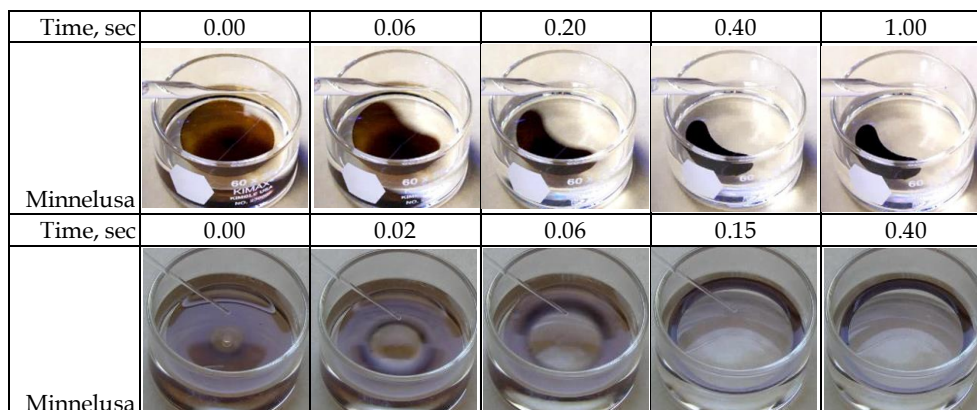


Figure 4. Retraction of a spilled thin film of Minnelusa crude oil after placement of a drop of 500 ppm aqueous BIO-SOFT® N91-8 solution at the side (a) or centre (b) of a glass beaker

The bottom row of photographs in Figure 4, was obtained after placement of a drop of 500 ppm aqueous BIO-SOFT® N91-8 solution at the center of the thin oil film that covered the entire water surface. This caused rapid outward retraction of the oil to form a ring of oil at the perimeter of the glass beaker. Build-up of the thickness of the ring can be clearly seen after 0.02 and 0.06 sec as the oil film retracts. The retraction is complete after 0.40 sec.

Aging of thin films of crude oil on the surface of water

A drop of Lustre crude oil spread quickly ($S=28$ mN/m); a thin oil film covered the entire surface of seawater in a glass beaker within a second. The thin oil film retracted quickly (<3 sec) when a drop of the aqueous 500 ppm BIO-SOFT® N91-8 solution was added, as shown by the series of photographs in the first row of Figure 5.

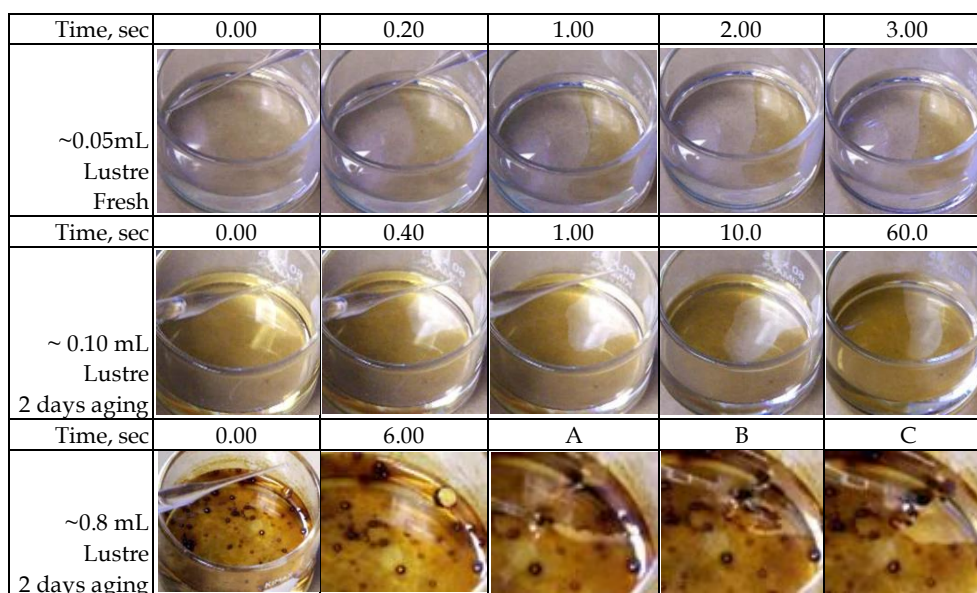


Figure 5. Retraction of a) fresh and b) ~0.1 mL and c) ~ 0.8 mL evaporated thin films of Lustre crude oil by addition of a drop of 500 ppm BIO-SOFT® N91-8 solution; a semi-rigid film was formed after a thicker film of the crude oil was allowed to evaporate for two days.

For the photographs shown in the second row, the volume of Lustre crude oil was doubled (~0.10 mL). After spreading, the beaker was left open in a fume hood for two days so that lighter components of the oil were lost by evaporation. The retraction of the aged thin film caused by a drop of 500 ppm BIO-SOFT® N91-8 solution was significantly slower than for freshly spread oil (see Figure 5b).

The photographs shown in the third row of Figure 5 were taken after approximately 0.8 mL of Lustre crude oil was allowed to spread on the seawater followed by evaporation for two days. A thin, semi-rigid film of aromatics, rich in polar asphaltenes and resins covers the water surface. A drop of BIO-SOFT® N91-8 solution was added along the glass wall. After 6 seconds, a small round hole formed in this semi-rigid film; the rest of the film remained intact. This semi-rigid film could be broken and rolled up using the tip of a glass pipette as shown in A, B and C of Figure 5c. This observation simulates how wave action can cause formation of tar balls at sea far from the spill location of the parent crude oil. These tar balls are highly adhesive because of their high aromatic content in the form of asphaltenes and resins.

DISCUSSION:

Nonionic surfactants having $n < 10$, and more particularly $3 < n < 8$, are expected to be advantageous because the surfactant molecules quickly accumulate at the air/water interface whereas for larger n values, spreading or diffusion is slower. Nonionic surfactants having branched hydrocarbon chains instead of linear chains are also believed to be advantageous since surfactants with branched hydrocarbon chains have less tendency to form micelles, and greater tendency to preferentially accumulate at the air/water surface. Nonionic surfactants are believed to be particularly advantageous because they have low critical micelle concentrations; thus less surfactant would be needed.

Blends of the anionic and nonionic surfactants may also be used to achieve a faster retraction rate of the spilled oil layer. Another option is to use water-soluble nonionic surfactants such as Tween 20 or 30 (Polysorbate surfactant 20 or 30). These surfactants are sugar derivatives; they are approved as food additives and are biodegradable.

The surfactant can be placed in a container that floats at the inner wall of an oil-spill control boom. The container can be designed to discharge a small amount of the surfactant into the water. Continuous discharge of small quantities of surfactant adjacent to the inner wall of a deployed boom will prevent spreading of crude oil and also prevent the oil from migrating over the boom surface, thereby eliminating or greatly reducing adhesion of crude oil to the deployed boom. The surfactant in the container can be mixed with fine solid materials such as kaolin and/or talc clay minerals to control the rate of release into water. Clay minerals not only allow slow release of surfactant; they also will become an integral part of the surfactant mono-layer which prevents spreading. This further improves the mechanical properties of the surfactant layer such that the retraction efficiency and durability is significantly improved.

CONCLUSIONS:

The combination of low surface and interfacial tension values for crude oil promotes rapid spreading of crude oil on seawater when an oil spill occurs. Spreading of the crude oil can be prevented or at least greatly reduced by lowering the air-water surface tension. This can be achieved, for example, by use of a very low concentration of water-soluble surfactant.

After crude oil has spread over the seawater surface and the lighter components have evaporated, the remaining oil is highly viscous and semi rigid. Coagulation of the oil provides a possible explanation of how sticky tar balls are found far from the location of the spill. The tar balls are sticky because of their high aromatic content in the form of asphaltenes and resins.

Laboratory experiments indicate that a floating oil control boom that disperses water-soluble surfactant would be highly effective in reducing the spreading of oil and greatly reducing adhesion of crude oil to the deployed boom. The surfactant can also be mixed with fine solid materials for controlled release of the surfactant.

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