

Spreading and Retraction of Spilled Crude Oil on Sea Water

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1. Introduction

The spreading of a liquid as a thin film on another liquid has fascinated the pioneers of modern surface science for over two centuries, including two pioneering women scientists, Agnes Pockels and Katharine B. Blodgett (Rayleigh & Pockels, 1891; Rayleigh, 1899; Harkins & Feldman, 1922; Harkins, 1941; Langmuir, 1933; Blodgett, 1935; Transue et al., 1942; Zisman, 1941a, 1941b, & 1941c; Shewmaker et al., 1954; Derrick, 1982; Covington, 2011). Davies & Rideal (1961) noted, "As long ago as 1765 Benjamin Franklin observed that olive oil spreads over water to a thickness of 25 Å". Harkins & Feldman (1922) defined the spreading coefficient, S , as:

$$S = W_A - W_C \quad (1)$$

thus a liquid will not spread if its work of cohesion W_C is greater than the work of adhesion W_A for the interface of the liquid and another liquid or solid upon which spreading is to occur. The W_A and W_C values are related to interfacial tensions by;

$$W_A = \gamma_a + \gamma_b - \gamma_{ab} \quad (2)$$

$$W_C = 2\gamma_b \quad (3)$$

and the spreading coefficient can be defined as;

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) \quad (4)$$

Here, b represents the liquid for which spreading upon a is under consideration. The validity of equation (4) was confirmed by the spreading behaviour of 89 organic liquids on water. The description by Harkins & Feldman (1922) of the effect of placing a drop of oleic acid at the centre of a lens of petroleum (refined) oil on the water surface is of particular interest. "The lens is broken up into a great number of fragments which seem to be projected with almost explosive violence toward the edges of the tray".

Effects of polar compounds on spreading of mineral oil on water were investigated in detail by Zisman (1941a, 1941b). Fatty acids and amines having over 13 carbon atoms per molecule adsorbed permanently at the oil-water interface if the pH of the water was adjusted to values greater than 10.5 or less than 3, respectively. Ionization of the adsorbed fatty acid or amine molecules caused the petroleum oil to spread as a thin disk of diameter directly proportional to the amount of fatty acids or amines in the oil. This observation provided an estimate of the cross-sectional area of adsorbed molecules at the interface. The results were consistent with the conclusions of Danielli on the effect of pH on the interfacial tension lowering for oleic acid adsorbed at the brombenzene-water interface (Danielli, 1937).

Zisman (1941a) also demonstrated that acids and amines of lower molecular mass would spread out from the leading edge of the oil lens across the water surface, so that 5 of the oil slowly rises. This edge diffusion was tracked visually by spreading a small amount of hydrophobic talc particles on the water surface. A schematic diagram of an apparatus used for measuring spreading rates and edge diffusion can be found in Davies & Rideal (1961).

The phenomenon of interfacial tension lowering was applied to a method for recovering residual oil from an oil reservoir (Squires, 1921; Atkinson, 1927). There are now numerous reports on laboratory research and field testing of caustic flooding. The subject was reviewed by Johnson (1976) and Mayer et al. (1983). The range of pH over which fatty acids cause interfacial tension change occurs is about 3 units of pH more alkaline than the range over which dissociation occurs in the bulk phase (Zisman, 1941a & 1941b; Danielli, 1937). The dissociation behaviour of the ionizable charge groups as a function of both bulk pH and electrolyte concentration was shown to be quantitatively predictable by the Ionizable Surface-Group Model (Takamura & Chow, 1985; Chow & Takamura, 1988).

Langmuir observed that low levels of calcium or magnesium ions prevented the spreading of oil droplets containing stearic acid (Langmuir, 1936). Zisman (1941a) conducted systematic studies of the effects of various polyvalent metallic ions and confirmed that rigid films were formed by the salts of the fatty acids at the oil/water interface. The amount of the metallic salt necessary to cause rigidity of the interfacial film was found to depend on the pH and the concentration of the acid in the oil. This behaviour closely resembles the formation of visco-elastic films at the crude oil/brine interfaces. The physical properties of calcium surfactants are the topics of a recent review article (Zapf et al., 2003). There have been many studies of the effect of interfacial film properties on the snap-off of oil blobs in porous media during the course of water-flooding (Chatzis et al., 1983; Laidlaw & Wardlaw, 1983; Yu & Wardlaw, 1986). The presence of visco-elastic films is a prime parameter in the stability of water-in-crude oil emulsions (Sjöblom et al., 2003).

Crude oil spreads rapidly over sea water due to the rather high values of the spreading coefficient (25-35 mN/m) (Garrett & Barger, 1970). The use of water-insoluble monomolecular films can be used to compress spilled oil into lenses of increased thickness that occupy smaller surface area, and can be retrieved mechanically (Zisman, 1943; Barger & Garrett, 1968; Garrett & Barger, 1970). In the current paper, the spreading behaviour of drops of heptane-decane-toluene ternary mixtures on the surface of water is modelled by molecular dynamics calculations. Special attention is given to the distribution of light alkane and aromatic molecules at the air/oil/water three phase line of contact. The conclusions are consistent with the results of extended detailed experimental studies of spreading and retraction of crude oil on sea water.

2. Theoretical background

The surface tension of the liquid arises from intermolecular attraction at the surface region. For liquid alkanes, this intermolecular attraction is entirely due to London dispersion forces, thus

$$\gamma_o = \gamma_o^d \quad (5)$$

where γ_o is the surface tension of the alkane oil and the superscript, d, designates the dispersion force contribution (Fowkes, 1964) which is a direct function of the refractive index of the liquid (Hunter, 1986). As seen in Figure 1, both the surface tension and refractive index of alkanes are linear functions of density.

The surface tension of water is the sum of a dispersion forces contribution, γ_w^d , and a polar (hydrogen bonding) forces contribution, γ_w^p ;

$$\gamma_w = \gamma_w^d + \gamma_w^p \quad (6)$$

and γ_w^d and γ_w^p are 21.8 and 51.0 mN/m, respectively at 20°C (Fowkes, 1964). Water molecules in the oil/water interfacial region are attracted towards the interior of the water phase by water-water interactions (dispersion forces and hydrogen bonding) and towards the oil phase by oil-water interactions (dispersion forces only); likewise, oil molecules at the interfacial region are attracted to the oil phase by oil-oil dispersion forces and to the water phase by oil-water dispersion forces. The interfacial tensions were related to the geometric means of the oil-oil and water-water intermolecular interactions (Girifalco & Good, 1957);

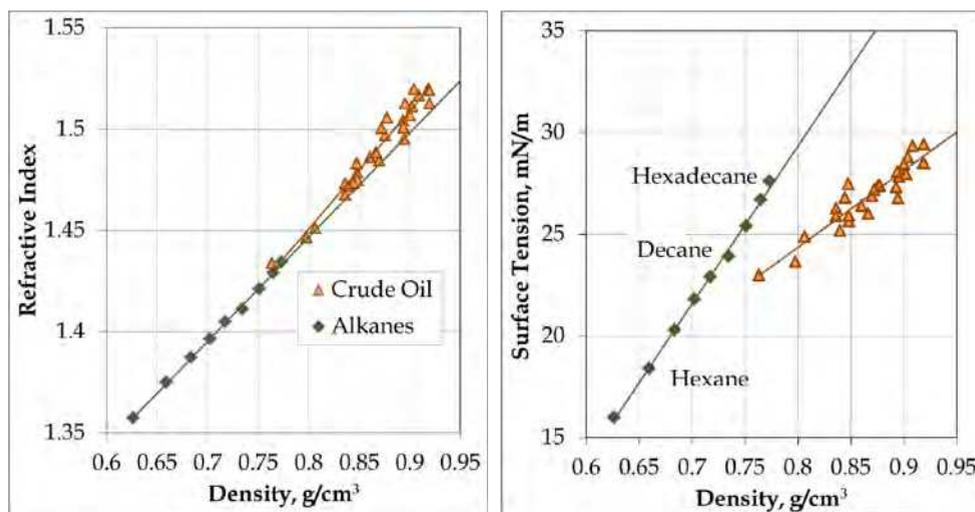


Fig. 1. Refractive index and surface tension of alkanes as a function of their density (solid diamonds). The same relationships for 23 crude oils are also shown with solid triangles. See details in the text.

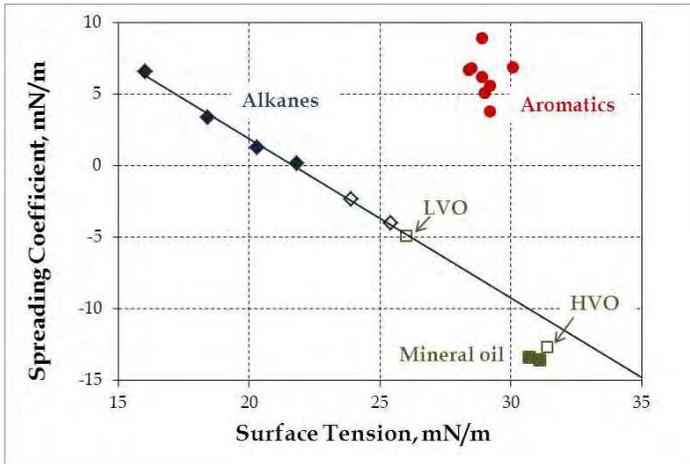


Fig. 2. Relation of spreading coefficient to surface tension of oils. Solid diamonds and circles are measured S for pure alkanes and aromatics, respectively (Pomerantz et al., 1967), other points are calculated values from γ_o and γ_{wo} data: open diamonds for alkanes (Girifalco & Good, 1957), solid squares for mineral oils referred to as “Squibb” and “Stanolax” (Harkins & Feldman, 1922), open squares for low and high viscosity mineral oils (3.9 and 173 mPa-s for LVO and HVO, respectively).

$$\gamma_{wo} = \gamma_w + \gamma_o - 2\sqrt{\gamma_w^d \gamma_o^d} \tag{7}$$

Substituting equation (6) and (7) into (4):

$$S = 2\left(\sqrt{\gamma_w^d \gamma_o^d} - \gamma_o\right) \tag{8}$$

Equation (8) shows that S for oil on water is a single-valued function of the surface tension of the oil (Fowkes, 1964) as shown in Figure 2.

The aromatic molecules are more hydrophilic than the saturated hydrocarbons (Pomerantz et al., 1967; Fowkes, 1964), resulting in lower interfacial tensions (e.g. 34.4 and 52.0 mN/m for benzene and n-heptane at 20°C, respectively). Thus, S values for the aromatics lie significantly above the straight line for the alkanes in Figure 2. Owens & Wendt (1969) have extended the equation (7) for the polar molecules:

$$\gamma_{wo} = \gamma_w + \gamma_o - 2\left(\sqrt{\gamma_w^d \gamma_o^d} + \sqrt{\gamma_w^p \gamma_o^p}\right) \tag{9}$$

Thus the spreading coefficient for the polar oil is now given as:

$$S = 2\left(\sqrt{\gamma_w^d \gamma_o^d} + \sqrt{\gamma_w^p \gamma_o^p} - \gamma_o\right) \tag{10}$$

Values of γ_o^d and γ_o^p for toluene are 27.8 and 1.3 mN/m, respectively (Clint & Wicks, 2001; Binks & Clint, 2002), and equation (10) predicts $S=7.3$ mN/m for toluene for $\gamma_o=29.1$ mN/m.

A small value of $\gamma_w^p=1.3$ mN/m for toluene results in rather substantial increase in S because of the strong polar forces of water ($\gamma_w^p=51$ mN/m).

Recent molecular dynamics simulation of the oil-water interface reveals a preferential accumulation of aromatics at the interface, due to the weak hydrogen bonding between hydrogen atoms of water and π -electrons of aromatics (Raschke & Levitt, 2004; Kunieda et al., 2010). In contrast, the low molecular mass saturates in multicomponent mixtures, e.g. mineral oil, preferentially accumulate at the surface and give low values of surface tension and the corresponding spreading coefficients fall below the line for alkanes.

Figure 1 includes the relationships for the refractive index and surface tension of the crude oil as a function of their density. Though refractive indices for the crude oil are slightly above the line for the alkanes, their surface tension values fall significantly below the line. This could be due to preferential accumulation of light end alkanes at the crude oil surface. Detailed physical properties of the crude oil can be found in Buckley & Fan (2007) and Loahardjo (2009).

This was confirmed by examining measured surface tensions of decane ($n\text{-C}_{10}\text{H}_{22}$) binary mixtures with hexadecane ($n\text{-C}_{16}\text{H}_{34}$), docosane ($n\text{-C}_{22}\text{H}_{46}$), and tetracosane ($n\text{-C}_{24}\text{H}_{50}$) (Rolo et al., 2002; Queimada et al., 2005). As seen in Figure 3, measured surface tension values of these binary mixtures at 20, 50 and 70°C, respectively, systematically fell below linear lines due to the surface excess of decane. The effect is less pronounced for lower molecular mass molecules and higher temperature. The measured surface tension of the decane/hexadecane is a linear function of the weight fraction at 60°C. The density of these binary mixtures is a linear function of the weight fraction, as expected for the ideal mixture at a wide range of temperature (Queimada et al., 2003).

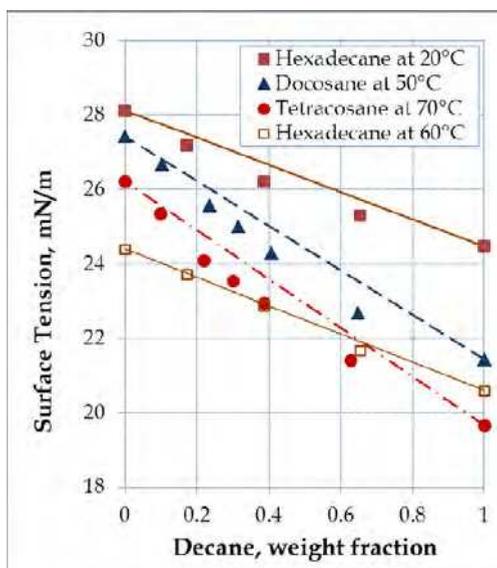


Fig. 3. Measured surface tension of decane binary mixtures with hexadecane, docosane, and tetracosane as a function of the weight fraction of decane.

3. 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 surface tension of the synthetic sea water (NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ of 28.0, 0.935, 1.56 and 11.56 g/L, respectively) of pH=6-7 was measured as a function of BIO-SOFT® N91-8 concentration 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 sea water. For the spreading experiment, approximately 35 mL of the synthetic sea water was placed in a glass beaker of 5.5 cm inside diameter and 3.5 cm height. A drop of the crude oil (~50 μL) was then placed on the water surface from a disposable glass pipette and spreading behaviour was video recorded.

4. Results and discussion

4.1 Molecular dynamics simulation of heptane-decane-toluene ternary mixtures

Spreading behaviour of a drop of the mixed solvent containing heptane, decane, and toluene of 250, 500, and 250 molecules, respectively was simulated on the surface of 18,458 water molecules. Detailed description will be given in a separate paper (Kunieda et al., 2012).

Results of the simulation are summarized in Figure 4 with a series of time lapse images, which show a spherical drop of 6.9 nm in diameter transforming to a liquid lens of maximum height of 4.1 nm after 2.97 ns of computational time. Only toluene molecules in the mixed solvent are shown in the third row of Figure 4, which clearly illustrates accumulation of toluene molecules at the water/organic solvent interface.

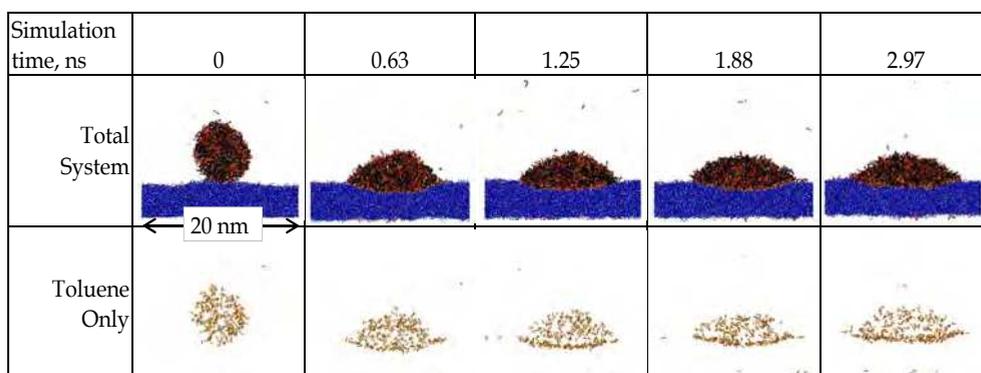


Fig. 4. Results of the molecular dynamics simulation of a mixed solvent of heptane, decane, and toluene of 0.25/0.50/0.25 mole fraction on the water surface at 25°C (the second row). Toluene molecules only in the mixed solvent are selectively shown in the third row.

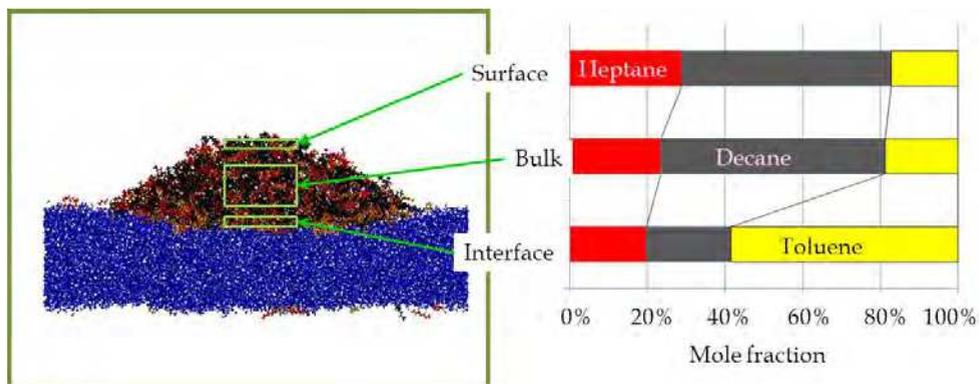


Fig. 5. Mole fraction of heptane, decane, and toluene in the bulk oil lens as well as the surface and interfacial regions after 2.97 ns computational time.

Changes in composition of the mixed solvent in the bulk, and the surface and interfacial regions are illustrated in Figure 5, which clearly demonstrates the preferential accumulation of toluene molecules at the water/oil interface; 0.25 in the bulk to slightly less than 0.6 mole fraction at the interface. Here, the interfacial region is defined as oil molecules which are at least one hydrogen atom within 0.3 nm from water molecules. The figure also confirms the surface excess of heptane against decane molecules.

4.2 Spreading behaviour of model binary and ternary mixtures on water

Density and surface tension of toluene-heptane, toluene-decane, and heptane-decane (add comma) binary mixtures were measured and reported in a previous paper (Kunieda et al., 2012). Figure 6(a) illustrates measured densities of the binary mixtures as a function of the weight fraction of either toluene or decane. The relationship for the binary mixture of alkanes (heptane and decane) follows the linear relationship against the weight fraction of decane, indicating no change in the volume upon mixing as for an ideal mixture. In comparison, those for the alkane-aromatic binary mixtures deviate systematically from the linear relationships towards lower densities, indicating the excess volume of alkanes-aromatic mixtures as reported by Qin et al. (1992). Solid diamonds in the figure represent the molecular dynamics simulation predicted density of toluene-heptane binary mixtures, which are in good agreement with measured values. This confirms that the molecular dynamics adequately simulate interactions between toluene and heptane in the bulk solution.

The measured surface tension of these binary mixtures is plotted against the weight fraction of either toluene or decane in Figure 6(b). The γ of a blend of alkanes, with small difference in molecular weights, follows a linear relationship against weight fraction. The same figure demonstrates pronounced reduction in surface tension from ideality of the alkane-aromatic binary mixtures. For decane/toluene, nearly half of the reduction in the surface tension of toluene occurs with addition of only 0.28 weight fraction (0.20 mole fraction) of decane. These observations are consistent with preferential accumulation of alkanes at the oil/air surface against the aromatic as shown in Figure 5 and also discussed in Kunieda et al. (2012).

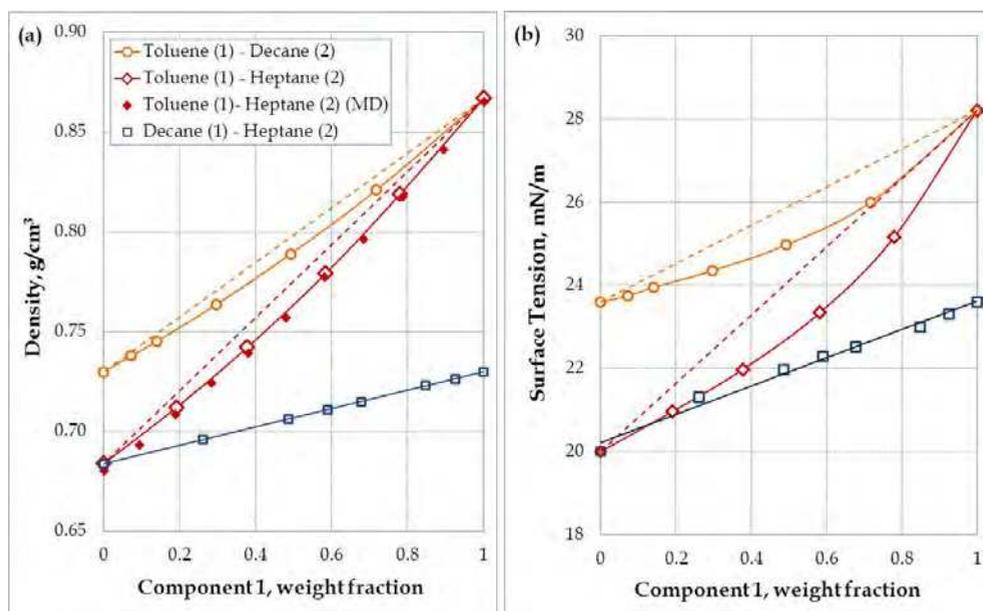


Fig. 6. Measured density (a) and surface tension (b) of toluene-heptane, toluene-decane, and decane-heptane binary mixtures as a function of the weight fraction of toluene or decane. The density of the binary mixture of alkanes is a linear function of the weight fraction, indicating an ideal mixture.

The interfacial tension of these binary mixtures was also measured against water at pH=6-7, and the spreading coefficient was calculated using equation (4). Results are summarized in Figure 7 by plotting calculated S against the surface tensions of the mixtures. Measured interfacial tensions of toluene, heptane, and decane are 35.2, 50.1, and 50.0 mN/m, respectively, which are about 2 mN/m lower than literature values even after removing polar components by flow through silica gel and alumina columns up to six times until the interfacial tension values were constant. Points for the heptane-decane binary mixture follow the linear relationship for a series of alkanes from the literature as discussed in Figure 2. Slightly lower values of the measured interfacial tension than the literature values of decane and heptane causes a slight deviation to larger S than the literature relationship.

The relationships, based on measurements for the toluene-decane and toluene-heptane binary mixtures, are highly non-linear with respect to composition, especially at above 0.4 mole fraction of toluene (see Figure 7). The S of pure toluene is 9.1 mN/m; addition of as much as 0.6 mole fraction of heptane has no significant effect on the spreading behaviour because $S=9.5$ mN/m for this mixture. The maximum, $S=10.3$ mN/m, is observed at 0.6-0.8 mole fraction of toluene. Thus, the binary mixture spreads more readily than either of the pure liquid components. The figure also shows addition of as much as 20% mole fraction of decane to toluene has no significant effect ($S=9.0$ mN/m). This is especially remarkable since $S=-2.1$ mN/m for the pure decane.

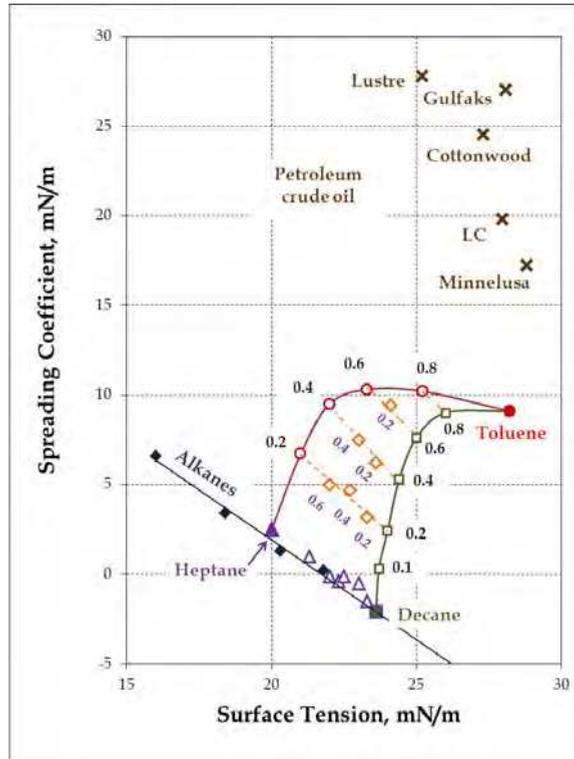


Fig. 7. Calculated spreading coefficient of toluene-heptane (circle), toluene-decane (square), and heptane-decane (triangle) binary systems as well as their ternary mixtures (open diamond). Numerical values beside data points for the binary mixtures represent the mole fraction of toluene for the binary mixtures, and mole fraction of heptane for the ternary mixtures. The same relationships for five crude oils tested for spreading behaviour on sea water are also included (cross).

Spreading coefficients for the ternary mixtures of toluene-heptane-decane are also included in the same figure. Dashed lines for the constant mole fraction of toluene are almost parallel to the linear relationship for the alkanes. The heptane-decane fractions merely affect the surface tension of the ternary mixtures and the fraction of toluene in the mixture determines the interfacial tension. $S=9.4$ mN/m for the ternary mixture of 0.2/0.2/0.6 mole fraction of decane/heptane/toluene, respectively, which is 0.3 mN/m higher than S for pure toluene.

These observed complexities of the spreading behaviour of the binary and ternary mixtures result from specific adsorption of the toluene and heptane at the oil/water and oil/vapor interfaces, respectively, as predicted by the molecular dynamics simulations (Figure 5).

4.3 Spreading of crude oil on sea water

Five crude oils of widely different properties were selected to examine their spreading behaviour on synthetic sea water at room temperature. Some physico-chemical properties of

these crude oils at 20°C are listed in Table 1 together with the calculated spreading coefficient (S) from equation (4) using their surface and interfacial tensions and $\gamma_w=73.5$ mN/m. Additional properties of these crude oils can be found in Buckley & Fan (2007) and Loahardjo (2009). Relationships between the surface tension and S are also included in Figure 7. Values of S for the crude oil are 2-3 times larger than the aromatics, mostly because of their low interfacial tensions. This suggests polar contributions of $\gamma_{oP}=1.5-3.9$ mN/m for the crude oils instead of 1.3 mN/m for toluene, suggesting the presence of weak accumulation of polar molecules in the resins and asphaltenes fractions at the oil/sea water interface at pH=6-7. In comparison, the reported value of γ_{oP} for 1-undecanol, $C_{11}H_{23}OH$, is as large as 20 mN/m (Binks & Clint, 2002). Detailed discussion of the correlation between the chemical composition of the crude oil and interfacial tension can be found in (Buckley & Fan, 2007). van Oss et al. (1988) have proposed correlating the polar component to the acid-base interactions, and this could certainly be applicable to the crude oil/water interface.

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

¹ against sea water at pH=6-7

Table 1. Selected physico-chemical properties of five crude oils used for the spreading experiments on the sea water. All measurements are at 20°C.

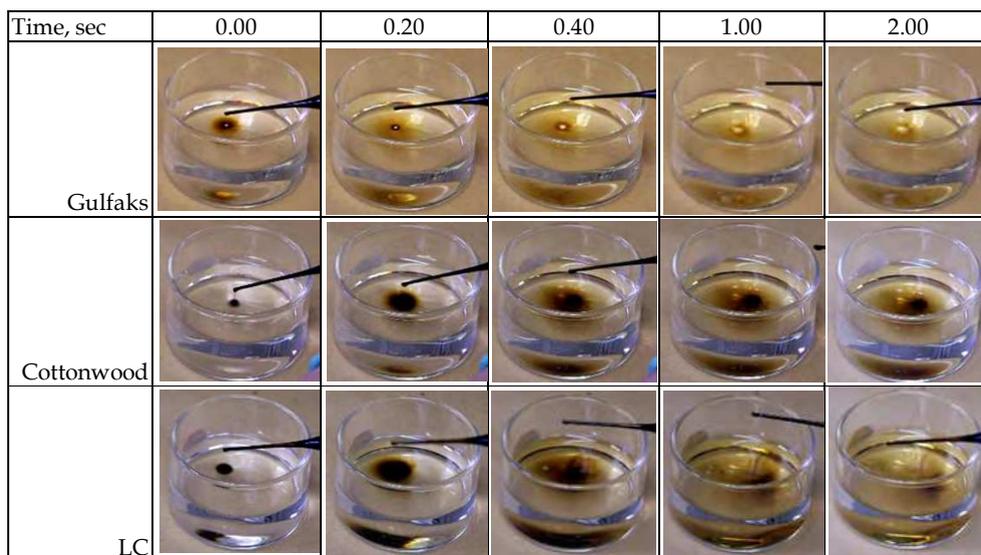


Fig. 8. Spreading behaviour of a drop (~50µL) of selected crude oils on sea water at 20°C.

Spreading behaviour of three crude oils; Gulfaks, Cottonwood, and LC are summarized in Figure 8 as a series of photographs illustrating the initial spreading of the crude oil on sea water. Calculated spreading coefficients for these crude oils are much higher than for pure alkanes and aromatics of similar γ_o , and range from 17 mN/m to 28 mN/m, as shown in Table 1. All of the tested crude oils spread rapidly on the sea water surface as a thin layer. The relationship between the thickness of the spreading oil as a function of S and density has been formulated by Langmuir (1933). Cochran & 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.

4.4 Control of the spreading of crude oil on sea water

Even a very low level of surfactant concentration, especially a non-ionic, is known to effectively lower the surface tension of water. Addition of as little as 30 ppm BIO-SOFT® N91-8 lowered γ_w of the sea water by 29 mN/m from 73 to 45 mN/m, (see Figure 9(a)). Figure 9(b) represents the measured interfacial tension of 5 crude oils as a function of the concentration of the same non-ionic surfactant. The γ_{wo} of the crude oil/sea water interface is already low in the absence of this non-ionic surfactant due to adsorbed polar components as discussed above. The γ_{wo} of Minnelusa oil is reduced only 8 mN/m, from 27 to 19 mN/m, with the same level of BIO-SOFT® N91-8 concentration. Detailed discussion on the interfacial tension and the micellar structure of the surfactant molecules at the oil/water interface can be found in Hoffmann (1990).

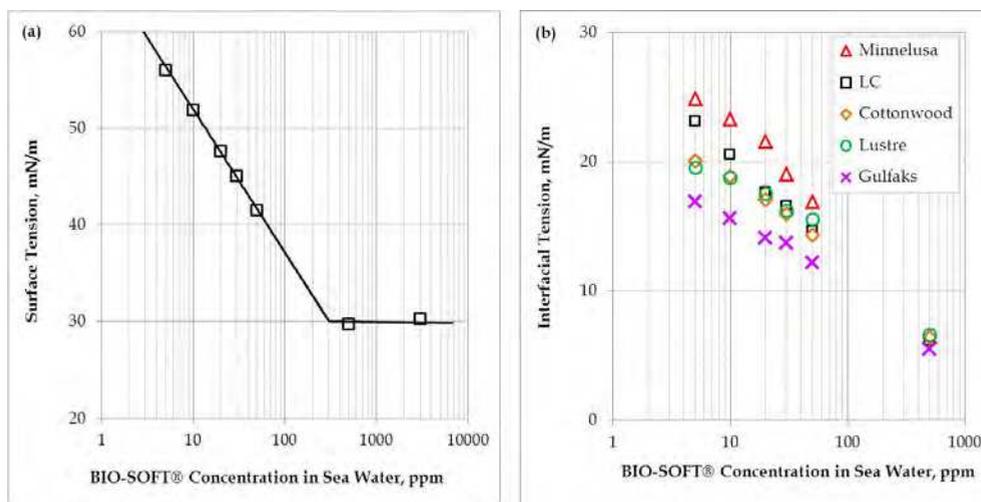


Fig. 9. The surface tension of the sea water (a) and interfacial tension of 5 crude oils (b) as a function of the non-ionic surfactant, BIO-SOFT® N91-8, concentration.

Equation (4) suggests 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 sea water. The spreading coefficients for five crude oils were calculated as a function of BIO-SOFT® N91-8

concentration in Table 2. The S values in the table were calculated using measured γ_{wo} of each crude oil against sea water and for sea water with a given concentration of BIO-SOFT® N91-8.

Crude oil	S (with γ_{wo} of sea water)					Crude oil	Initial Spreading Behavior				
	Sea water with BIO-SOFT®, ppm						Sea water 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
	S (with γ_{wo} of sea water/BIO-SOFT®)										
Lustre	28	11	8	5	4						
Gulfaks	27	11	8	5	3						
Cottonwood	25	9	6	3	2						
LC	20	5	3	2	0						
Minnelusa	17	2	0	-3	-3						

Table 2. Calculated S and observed spreading behaviour of five crude oils on sea water. INT indicates that slow spreading of the oil droplet was still observed. S was calculated using the γ_{wo} of sea water in the presence (top) and absence (bottom) of BIO-SOFT® N91-8.

The spreading behaviour of Minnelusa crude oil over sea water shown in Figure 10 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. Observed spreading behaviour shown in Table 2 agrees better with the S calculated using γ_{wo} against sea water instead of sea water with a given amount of BIO-SOFT® N91-8. In the table, INT indicates that some slow spreading of the oil droplet still occurred as seen in Figure 10. This observation suggests that the surfactant molecules are not yet adsorbed at the rapidly spreading frontal perimeter of the oil/sea water interface.

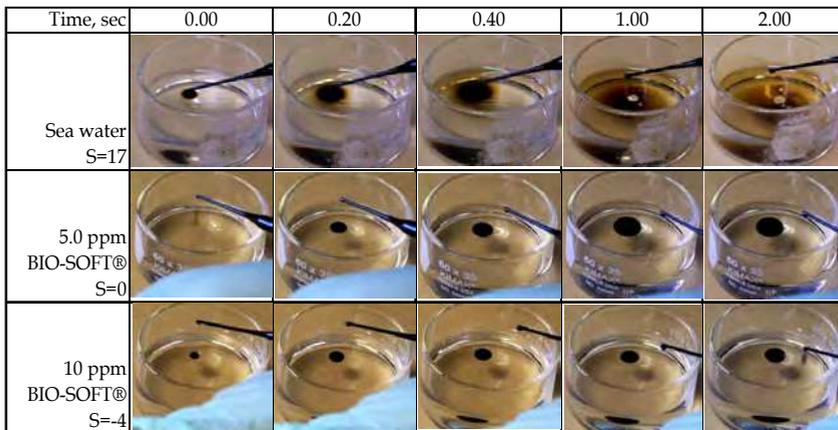


Fig. 10. Spreading behaviour of Minnelusa crude oil on sea water in the absence and the presence of 5 and 10 ppm BIO-SOFT® N91-8.

4.5 Retraction of spilled crude oil

Results shown in Figure 10 and Table 2 suggest that placement of a small amount of the aqueous non-ionic surfactant solution would effectively cause retraction of the spilled crude oil on the water surface. This is demonstrated in Figure 11, where a drop of Minnelusa crude oil ($S=17$ mN/m) quickly spread on the sea water surface (time=0 sec). The thin film of crude oil has quickly retracted to the opposite side after a drop of 500 ppm aqueous BIO-SOFT® N91-8 solution was added near the side wall of a glass beaker (top photographs). The lens of crude oil of (> 1 mm in thickness) can be skimmed mechanically from the open water surface (Cochran & Scott, 1971). The retraction of the thin film was confirmed for all of the five crude oils tested in this study.

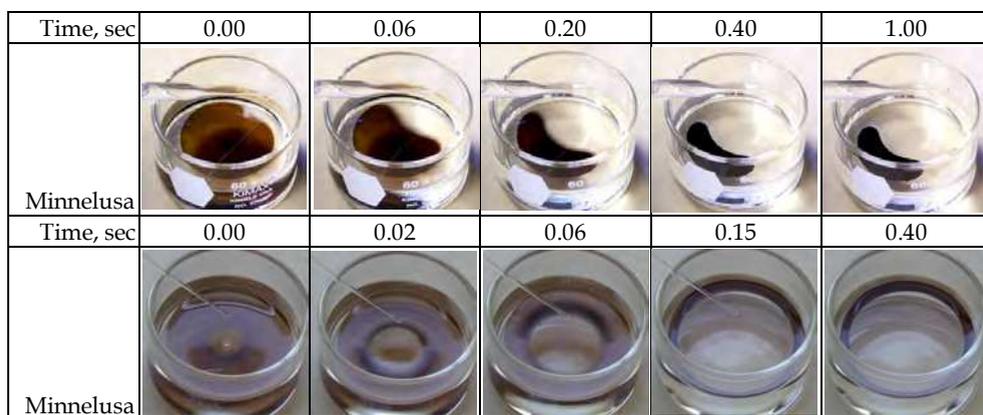


Fig. 11. Retraction of a spilled thin film of Minnelusa crude oil by addition of a drop of 500 ppm aqueous BIO-SOFT® N91-8 solution at the side (first row) or centre (second row) of a glass beaker.

At the bottom row of photographs in Figure 11, a drop of 500 ppm aqueous BIO-SOFT® N91-8 solution was placed at the center of the thin oil disc covering the entire water surface, causing rapid retraction of the oil outward toward the perimeter of the oil disc. Build-up of a slightly thicker oil ridge can clearly be seen after 0.02 and 0.06 sec as the oil film retracts. In this demonstration, the glass wall of the beaker restricts further spreading of the oil disc, resulting in formation of a narrow ring of the oil film at 0.40 sec. This oil ring would break-up under weak mechanical disturbance (i.e. wave action) to smaller size droplets.

The outer perimeter of the oil ring is facing toward the water of high surface tension, thus a high value of S , whereas the inner perimeter is associated with the water of lower surface tension (and $S < 0$). On an open water surface, the gradient in the capillary forces will cause rapid outward spreading of the thin oil film. This would result in break-up of the oil disc at the rapidly expanding outside perimeter of the thin oil disc as described by Zisman (1941a). This suggest the same chemical could act both as the retracting and dispersing agent based on the location of its placement; either in the oil or water phase.

4.6 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 sea water 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 12.

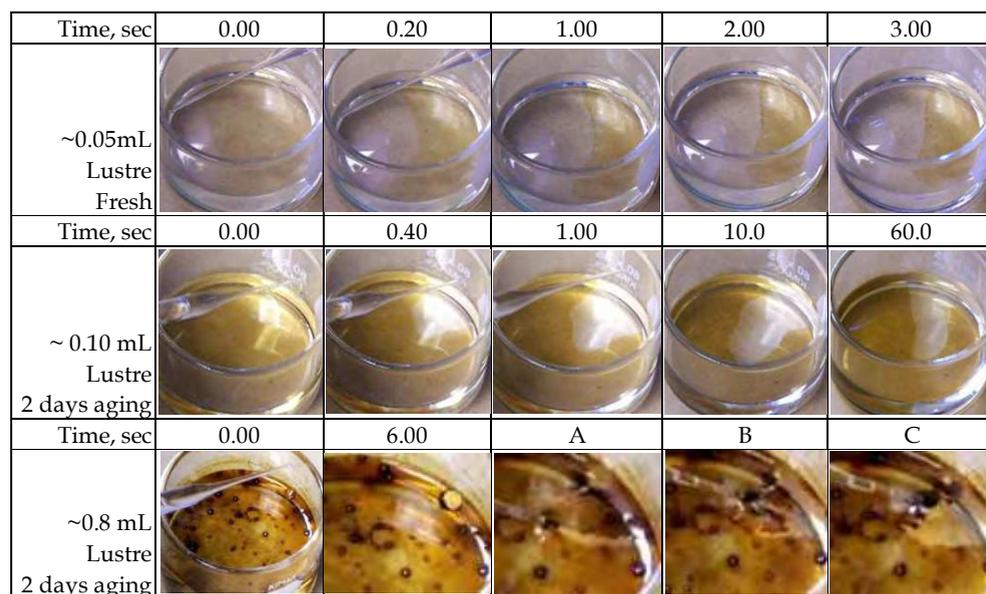


Fig. 12. Retraction of fresh and aged thin film of Lustre crude oil by addition of a drop of 500 ppm BIO-SOFT® N91-8 solution. A semi-rigid film was formed when a thicker film of the crude oil (with 0.8 mL of the oil instead of 0.05 and 0.1 mL) was aged for two days.

For the photographs shown in the second row, twice the amount (~0.10 mL) of Lustre crude oil was allowed to spread over the sea water surface and the beaker was left open in a fume hood for two days. 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 12).

The third row of photographs in Figure 12 were taken after, approximately 0.8 mL of Lustre crude oil was allowed to spread on the sea water surface followed by aging 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 the third row of Figure 12. This observation simulates how wave action can cause formation of tar balls at sea far from the parent spill of crude oil. These tar balls are very sticky because of their high content of aromatics in the form of asphaltenes and resins.

5. Conclusion

The surface tension of alkanes is the result of the London dispersion forces, which are directly proportional to density. When the surface tensions of a series of crude oils is plotted against their densities, they also follow a close-to-linear relationship but the values fall significantly below those for alkanes of the same density due to preferential accumulation of light end alkanes at the crude oil surface.

Molecular dynamics simulation of the aromatic-water interface reveals a similar preferential accumulation of aromatics at the interface, due to the weak hydrogen bonding between the hydrogen atoms of water and the π -electrons of aromatics. This explains why aromatic-water interfacial tensions (e.g. 34.4 mN/m for benzene at 20°C) are lower than those for alkane-water (e.g. 52.0 mN/m for n-heptane).

Aromatics that are preferentially accumulated at the crude oil-water interface will promote migration of asphaltenes and polar components in the crude oil toward the interface, resulting in further reduction in the interfacial tension between crude oil and sea water to below 30 mN/m. The combination of low surface and interfacial tension values for crude oil promotes rapid spreading of crude oil on sea water when an oil spill occurs. Light end alkanes evaporate quickly due to their low vapour pressure and a thin film of aromatics, rich in asphaltenes and resins, spreads ahead of the bulk crude oil over the water surface. The spreading action results in formation of tar balls far from the parent spill of crude oil. Spreading of the crude oil can be prevented or at least greatly reduced by lowering the surface tension of the water. This can be achieved, for example by use of a very low concentration of non-ionic surfactant.

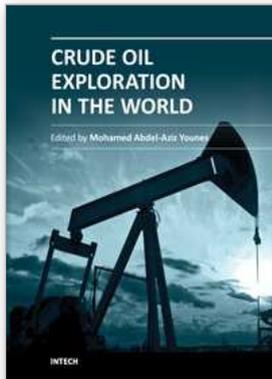
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