SUPPLEMENTARY INFORMATION

Switchable Anionic Surfactants for the Remediation of Oil-Contaminated Sand by Soil Washing

Elize Ceschia, Jitendra Harjani, Chen Liang, Zahra Ghoshouni Rahami, Tamer Andrea, R. Stephen Brown and Philip G. Jessop**

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, ON, Canada, K7L 3N6, Tel. (613) 533-3212. Fax (613) 533-6669. jessop@chem.queensu.ca

1 Experimental

1.1 Reagents and Instrumentation

CO_2 (99.9%, Praxair) and nitrogen (99.998%, Praxair) were used as received. Ottawa Sand was purchased from EMD Chemicals. North Sea crude oil was provided by Chevron Energy Technology Company; the properties of the oil are given in Table S1. All chemicals acquired from commercial sources were used as received unless specified. Deionized water was obtained using a Millipore Synergy UV (SYNSV0000) filtration system.

Switchable surfactants were synthesized in the laboratory. N'-octyl-N,N-dimethylamidine (C8) was prepared by the literature method.[1, 2] The sodium salt was made in-situ using sodium bicarbonate monohydrate during surfactant solution preparation.

The carboxylate salts of 4-octyloxybenzoic acid (**3b**) was prepared by mixing the acid with 1.1 equivalents of sodium hydroxide in water, refluxing for 4 h, cooling to 0 ˚C, and filtering. The white solid products were washed with cold water and then ether, dried under vacuum at 60 ˚C overnight, and crushed with a mortar and pestle. Sodium dodecanoate (**4b**) was purchased from Acros and used as received.

Conductivity was measured using a Jenway 470 Conductivity meter. Fluorescence data were acquired using a PTI Fluorimeter with an 814 Photomultiplier Detection System and LPS-220B Xenon Arc Lamp Power Supply. UV-Visible Spectroscopy data was obtained using an Agilent 8453 UV-Vis Spectrometer.

Table S1: North Sea Crude Oil Properties[25]

Property	Value
API Gravity	19.5
Specific Gravity	0.937
Viscosity at 40 ºC (cSt)	129
Viscosity at 100 ºC (cSt)	11.2

1.2 Syntheses

Synthesis of *n*-octyl 4-hydroxy-3-nitrobenzoate (**1b**): A mixture of 4-hydroxy-3-nitrobenzoic acid (5.00 g, 27.3 mmol), *n*-octanol (7.1 g, 8.62 mL, 54.6 mmol), *para*-toluene sulfonic acid (0.050 g) and toluene (200 mL) were refluxed for 24 h under a Dean-Stark trap to remove water by azeotropic distillation. After completion of the reaction, toluene was evaporated under reduced pressure (rotary evaporator) to obtain a thick mass. The resultant was diluted with diethyl ether (400 mL). A solution of potassium hydroxide (2.00 g, 35 mmol) in ethanol (95%, 40 mL) was added into the ethereal solution of the reaction mixture, this resulted in the formation of a dark orange solid. The solid was filtered through a sintered glass funnel, washed with diethyl ether (2 × 20 mL) and dried in a vented fume hood. The cold aqueous solution of this solid (200 mL of water) is gradually acidified with concentrated hydrochloric acid till the solution is acidic (pH paper). The acidification causes the precipitation of a solid or formation of an oily liquid that solidifies when cooled (*n*-octyl 4-hydroxy-3-nitrobenzoate, **1b**). Yield 87%.

^{1}H NMR (400 MHz, $CDCl_3$): 0.80-0.83 (t, *J* = 6.4 Hz, 3H), 1.22-1.36 (m, 10H), 1.67-1.74 (m, 2H), 4.25-4.28 (t, *J* = 6.6 Hz, 2H), 7.14-7.16 (d, *J* = 8.8 Hz, 1H), 8.15-8.18 (dd, *J* = 1.6 , 8.8 Hz, 1H), 8.73-8.74 (d, *J* = 2Hz, 1H), 10.81 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 13.83, 22.08, 25.45, 28.13, 28.61, 28.66, 31.23, 64.88, 119.36, 120.63, 126.58, 135.11, 136.69, 155.87, 163.99. IR (KBr): 3270, 2961, 2922, 2858, 1717, 1631, 1582, 1490, 1477, 1426, 1331, 1282, 1178, 1147, 1037, 1018, 971, 928, 864, 834, 761, 695, 636 cm^{-1}. UV: λ_{max} = 240 nm (ε_{max} = 57,400 dm^3 $mole^{-1}cm^{-1}$) and 336 nm (ε = 6265 dm^3 $mole^{-1}cm^{-1}$).

Synthesis of *n*-octyl 4-hydroxy-3,5-dibromobenzoate (**2b**):

A solution of 4-hydroxybenzoic acid (20 g, 143 mmol) and n-octanol (49.4 mL, 314 mmol) in toluene (50 mL) was refluxed for 18 h. The volatiles were removed under high vacuum at 150 ˚C. The resulting solid was dissolved in hexane and kept in a freezer to obtain white crystals of n-octyl 4-hydroxybenzoate in 89% yield.

A mixture of n-octyl 4-hydroxybenzoate (1.00 g, 4 mmol) and glacial acetic acid (10 mL) were stirred to obtain a clear solution. Sodium acetate (1.64 g, 20 mmol) was added and the mixture was allowed to swirl to obtain a clear solution. Next, a solution of Br_2 (2.56 g, 16 mmol) in glacial acetic acid (10 mL) was added gradually to the mixture, after which the mixture was allowed to stir at room temperature for 1 h. Acetic acid, HBr and Br_2 were removed from the reaction mixture by evaporation under reduced pressure in 3 h at 80 ˚C. The residue was mixed with 30 mL water which caused a light orange-brown liquid to separate from the reaction mixture. Subsequently, the reaction mixture was cooled to 0 ˚C and a solid compound was generated which is dissolved in solution of

Na_2CO_3 (2 g in 30 mL of H_2O). CO_2 was bubbled through the Na_2CO_3 solution to cause the regeneration of phenol. The procduct was filtered, washed with cold water, and air dried, giving *n*-octyl 4-hydroxy-3,5-dibromobenzoate in 81% yield (1.32 g).

^1H NMR (400 MHz, DMSO-d_6): 0.86 (t, *J* = 6.8 Hz, 3H), 1.2-1.35 (m, 10H), 1.62 (t, 2H, 6.6 Hz, 2H), 4.07 (t, J = 6.4 Hz, 2H), 7.74 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): 13.95, 22.06, 25.58, 28.38. 28.58, 28.63, 31.20, 63.20 (OCH_2), 114.07 (C-Br), 132.53 (arylC-H), 164.82 (C-OH), 165.65 (C=O). Ester-bound aryl quaternary carbon not observed. IR (KBr): 2956 (m), 2917 (m), 2853 (m), 1682 (s), 1647 (w), 1577 (s), 1479 (s), 1397 (m), 1340 (s), 1256 (s), 1140 (m), 967 (m). HRMS (EI) for $C_{15}H_{20}O_3Br_2$ Calculated: 405.9779. Observed: 405.9776.

1.3 Investigation of the switching process

NMR spectroscopic study of the switching of phenol **1b**: A solution of 46 mg (0.156 mmol) octyl 4-hydroxy-3-nitrobenzoate **1b** and 136 mg (1.28 mmol) Na_2CO_3 was prepared in 16.0 mL of D_2O. To this solution, 11.5 mg of $[Me_4N]I$ was added. The resultant solution was homogenized by sonication for 2 min. 1.00 mL of this solution was transferred (accurately using a Hamilton syringe, least count: 0.005 mL) into eleven different vials. A stir bar was introduced in the vials from 3 through 11. Vial 1 was the control solution, so it was not treated further. CO_2 was introduced into vial 2 for 5 min in order to "turn off" the surfactant. The CO_2 was introduced into vial via a needle that was not allowed to dip into the solution, but was held above the solution in such a way that the slow flow of CO_2 was allowed to interact with the surfactant solution only at the surface. The procedure required 5 min (or less in some cases). Increasing the surface area by slightly tilting the vial appeared to increase the rate of switching. The solution in vial 3 was first turned OFF with CO_2 treatment and then turned ON by heating the contents at 70 °C for 40 min (followed by addition of 0.50 mL of D_2O to make up for evaporative losses). The solution in vial 4 was first turned OFF with CO_2, then turned ON by heating the contents at 70 °C for 40 min (0. 50 mL of D_2O added) and finally turned OFF with CO_2. The remaining vials were treated with increasing numbers of ON and OFF cycles. NMR spectra were recorded. All the vials were tightly capped and left over night, to confirm the stability of the systems upon prolonged standing (Figure S1).

NMR spectroscopic study of the switching of phenol **2b**: A solution of 6.1 mg (0.015 mmol) **2b** and 0.6 mg NaOH (0.015 mmol) was prepared in 15 mL D_2O and 1.0 mM solution was obtained. The vial containing this solution was shaken for 10 min in order to obtain a homogenized solution. Aliquots (1 mL each) of this solution and a stir bar were introduced into 6 different vials using Hamilton syringes. Vial 1 did not enter in to ON/OFF cycle and it remained as the control solution. The solution in vial 2 was exposed to CO_2, as described above, for 10 min and filtered immediately because the acid form was prone to switch back to its anionic form. The solution in vial 3 was switched OFF by CO_2 flowing for 10 min and then turned ON by heating the vial at 60 °C for 30 min. Vial 4 was treated with CO_2, then heat, then CO_2 again, and then filtered right away. The solution in vial 5 was given two CO_2/heat cycles. Vial 6 was given two CO_2/heat cycles, a third CO_2 treatment, and then was filtered without delay. 1 mL of prepared 0.001 M DMF in D_2O was introduced in to each vial as an internal standard. After shaking the vials, the related ^1H NMR spectra were recorded.

Measurements of the pH of solutions of surfactant **1**: A solution of n-octyl 4-hydroxy-3-nitrobenzoate (0.221 g, 0.75 mmol) and NaOH (0.045 g, 1.13 mmol) was prepared in 150 mL of double deionized water and heated to 70 ˚C for 1 min to obtain a homogeneous 5 mM solution of **1a**. Aliquots of this solution (10.0 mL each) were transferred using a Hamilton syringe into eleven different vials 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11. The level of the solution in each vial was marked. Stirring bars were introduced in vial from 3 to 11. Vial 1 was the left alone to serve as the control solution. To turn the surfactant OFF, CO_2 was slowly bubbled through the solution for 10 min (this was marked by formation of light yellow solid precipitate). To turn the surfactant ON the solution was heating (while being stirred) in a preset oil bath at 70 ^{o}C for 1 h. The solution in vial 2 was turned OFF. The solution in vial 3 was first turned OFF and then ON. The solution in vial 4 was first turned OFF then ON and finally OFF. The details of the treatment given to individual vials are outlined in Table 1. After completion of the cycle, each vial was sealed with Parafilm and allowed to cool down to room temperature overnight. The pH was measured at 25 ˚C the next day.

A similar experiment using Na_2CO_3 as the base (Figure S1) rather than NaOH was visually identical, giving a strongly yellow homogeneous solution under air and a very pale yellow or colourless solution with a pale yellow precipitate under CO_2.

Figure S1. The switching of solutions of **1** and a base (either NaOH or, in this experiment, Na_2CO_3) between a homogeneous yellow solution of **1a** in water and a mixture of precipitated **1b** and decolorized solution. The first vial (far left) was never exposed to CO_2. The second vial was exposed to CO_2. The third was exposed to CO_2 and then the CO_2 was removed by a heat treatment. The vials further to the right were exposed to further such cycles. All vials were tightly capped after treatment and allowed to stand at room temperature for 18 h before the photograph was taken.

Measurements of the pH of solutions of surfactant **2**: A solution of octyl 3,5-dibromo-4-hydroxybenzoate (0.612 g, 1.5 mmol) and NaOH (0.09 g, 2.25 mmol) was prepared in 300 mL of double deionized water and heated to 70 ˚C for 1 min to obtain a 5 mM homogeneous solution of **2a**. Aliquotes (10.0 mL each) of this solution were transferred using a Hamilton syringe into eleven different vials and treated in the same way as the solutions of **1a** described above, with the exception that the heating times were changed from 1 h to 3 h.

Measurements of the pH of solutions of surfactant **3**: A solution of 4-octyloxybenzoic acid (0.375 g, 1.5 mmol) and NaOH (0.09 g, 2.25 mmol) was prepared in 300 mL of double deionized water and heated to 70 ˚C for 1 min to obtain a 5 mM homogeneous solution of **3a**. Aliquotes (10.0 mL each) of this solution were transferred using a Hamilton syringe into eleven different vials and treated in the same way as the solutions of **1a** described above, with the exception that the heating times were changed from 1 h to 3 h.

Measurements of the pH of solutions of surfactant **4**: A solution of sodium dodecanoate (0.333 g, 1.5 mmol) was prepared in 300 mL of double deionized water and heated to 70 ˚C for 1 min to obtain a 5 mM homogeneous solution of **4a**. Aliquotes (10.0 mL each) of this solution were transferred using a Hamilton syringe into eleven different vials and treated in the same way as the solutions of **1a** described above, with the exception that decarbonation temperature was 60 ˚C instead of 70 ˚C.

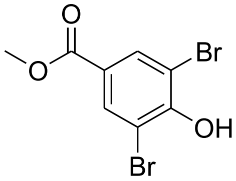
Measurements of the surface tension of solutions of surfactant **1**: The surfactant solution was prepared by combining 0.460 g (1.559 mmol) of octyl 4-hydroxy-3-nitrobenzoate **1** and 1.36 g (12.83 mmol) of Na_2CO_3 in 160 mL of H_2O to obtain a 9.7 mM solution. The resultant solution was homogenized by sonication for 2 min. 10 mL of this solution was transferred into thirteen vials (13 × 10 mL, vial numbers: 1, 2, 2^*, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12). The levels of solution in all the vials were marked. A stir bar was introduced in vials 2^* through 12. Vial 1 was the control solution, so it did not enter into the ON/OFF cycle. The standard procedure to turn the surfactant OFF was to slowly bubble CO_2 for 5 min. To turn the surfactant ON, the solution was heated at 70 ^{o}C for 40 min. The surfactant in vial 2 was turned OFF by slowly bubbling CO_2. The solution in vial 2^* was turned OFF with CO_2 and then stirred at room temperature (not capped) for 48 h. The solution in vial 3 was first turned OFF with CO_2 (bubbling for 5 min) and then turned ON by heating the contents at 70 ^{o}C for 40 min. The solution in vial 4 was first turned OFF with CO_2, then turned ON by heating the contents at 70 ^{o}C for 40 min and finally turned OFF with CO_2. The details of the treatment of the individual vials are presented in Table 1. All vials (excluding 2^*) were tightly capped (screw cap and parafilm used to ensure no leakage/displacement of gases) and left at room temperature for 18 h to confirm the stability of the systems in both the ON and OFF forms upon standing (Figure 3). The volumes of all the vials are corrected with water to match the originally marked level. All the solutions are homogenized and the contents of vials with even numbers are filtered (passed through a Kimwipe^{TM} plug in a pipette) to obtain a clear solution. All the even numbered vials were clear, therefore did not require filtration.

The tensiometer was first calibrated with water. The value obtained for water (72 dynes/cm) was acceptable within experimental error. For test solutions as well as for standard solutions, the surface tension was measured in triplicate. The three values of surface tension for each solution remained within ±1 dynes/cm. For each solution, the average value of the three measurements is presented in the tables. To confirm that the instrument had not drifted during the measurements, the surface tension of water was recorded again after the experiment and was found to be 71 dynes/cm.

Measurement of the pK_a of compound **2c**: Methyl 3,5-dibromo-4-hydroxybenzoate (obtained commercially) (0.053 g) was dissolved in 25 mL of MeOH:water 70:30 by volume to obtain a 6.90 mM solution. 100 µL of **2c** solution was added to 5 mL of the MeOH : water mixture followed by 70 µL HCl (20 mM, Fisher certified) and titrated with standardized soduim methoxide solution in the same solvent mixture. The ionic strength was controlled by adding KCl. The measurement was performed twice.

The titration was performed with a Metrohm, 798 MPT Titrino Autotitrator, equipped with an Accumet model 13-620-183 combination glass electrode calibrated with Fisher certified standard aqueous buffers (pH 4.00 and 10.00). The temperature was kept at 25.0 °C using a water bath. Sodium methoxide titrant (12.85 mM) was prepared in 70 : 30 MeOH : water (by volume) and was standardized by titrating an aliquot of Fisher certified $HCl_{(aq)}$, with the endpoint taken to be pH 7.0.

The pK_a in the working solvent (${}_{w}^{s}pKa$) was measured to be 6.02 ± 0.02. The solvent corrected pK_a (${}_{s}^{s}pKa$) was calculated by including a correction factor ($\delta = 0.175$) for the solvent mixture.[3] The pK_a value for **2c** in pure water (${}_{w}^{w}pKa$) was calculated from the ${}_{s}^{s}pKa$ by including published[4] correction factors for phenol groups in the appropriate methanol : water volume fraction.



2c

1.4 Emulsion Stability Tests

Emulsions stabilized by **2a**: The emulsion solution was prepared by adding 6.1 mg (0.015 mmol) of octyl 3,5-dibromo-4-hydroxybenzoate and 0.6 mg (0.015 mmol) NaOH to 4 mL 1-octanol and stirred, then 2 mL H_2O was added to the mixture. The vial containing octanol, surfactant and water was shaken using an automatic wrist-action shaker (Burrell Model 75) for 15 min and photographed right after shaking and after a waiting period of a) 5 min, b) 1h, c) 20 h (Figure S2). The same experiment was also performed in CO_2-saturated water under an atmosphere of CO_2.

Emulsions stabilized by **4a**: Sodium dodectanoate (0.1 g, 0.45 mmol) was combined and stirred with 4 mL 1-octanol. Then 2 mL H_2O was added to the mixture (test 5). The vial containing octanol, surfactant and water was shaken using the automatic shaker for 15 min and photographed after waiting period of a) 5 min, b) 15 min, c) 30 min, d) 20 h.

In another experiment, 0.1 g (0.45 mmol) surfactant was combined with 4 mL 1-octanol. After stirring the solution, 2 mL water was added to the solution and CO_2 gas was bubbled through the solution for 1 h. The vial was shaken in the automatic shaker for 15 min and photographed after waiting period of a) 5 min, b) 15 min, c) 30 min, d) 20 h. (figure S3)

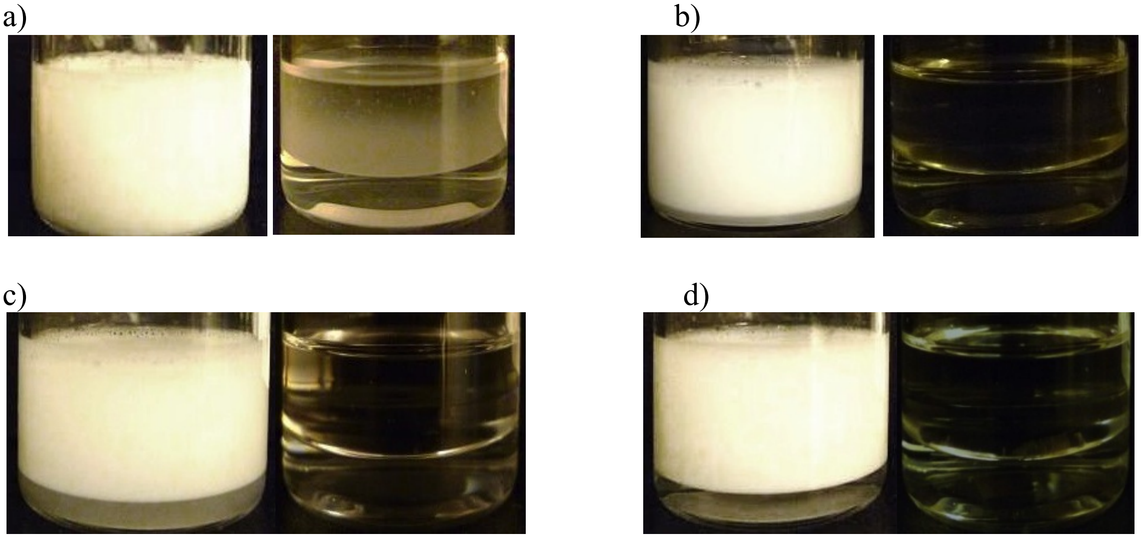


Figure S2. Photographs of 2:1 (v/v) octanol/water mixtures containing **2a**. Each pair shows the solution prepared without (left vial) and with CO_2 (right vial), after 15 min of shaking followed by a waiting period of a) 0 min, b) 5 min, c) 1 h, d) 20 h. Conditions: room temperature, 4 mL 1-octanol, 2 mL water, 15 μmol each of NaOH and **2b**.

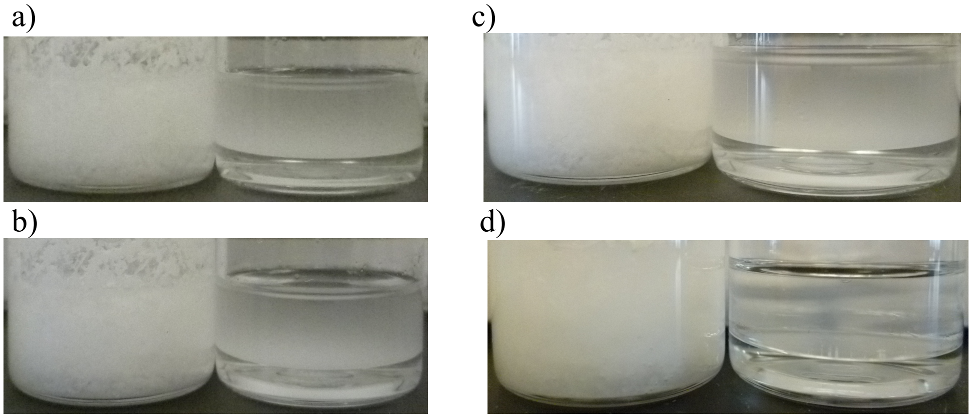


Figure S3. Photographs of 2:1 (v/v) octanol/water mixtures containing sodium dodecanoate (225 mM in the aqueous phase) under air (left vial) or saturated with CO_2 (right vial) after 15 min of automated shaking followed by a waiting period of a) 5 min, b) 15 min, c) 30 min, d) 20 h.

1.5 Artificial Sand Contamination & Weathering

Sand samples were prepared to achieve a pre-weathering contamination level of 3.8 ± 0.1 wt% oil. North Sea crude oil (3.7 - 4.8 g) was added to a pre-weighed 400 mL beaker. Tetrahydrofuran (THF) was added to solubilize the oil. Enough Ottawa Sand was then added (94 - 127 g) to achieve the desired weight percent contamination on the sand.

The beaker was left uncovered overnight at room temperature to allow the THF to evaporate. Afterwards, the sand was broken up and mixed in the beaker. The beaker was then left uncovered for a further time period so that the total evaporation time was at least 24 h.

After the sand was left to sit for at least 24 h, it was transferred to a pre-weighed Petri dish which was placed into an oven at 110 ºC for another 24 h.[5] The Petri dish was removed and cooled to room temperature. The Petri dish and sample mass was recorded and the sand was transferred into a 100 mL amber vial for storage. The contamination level of this “weathered” sand ranged between 2.6 and 3.1 wt % oil.

Table S2: Contamination levels of the sand before and after weathering.[a]

Batch Number	Batch Weight (g)	Oil Mass Before Weathering (g)	Oil Mass After Weathering (g)
1[b]	40.9	1.6	1.0
2	89.8	3.3	2.3
3	127.2	4.7	4.0
4	101.7	3.9	3.0

[a]Air dried for 24 h followed by heating at 110 ºC for 24 h. “Batch weight is the mass of sand and oil combined. [b]This batch was split into two portions, only one of which was weathered.

1.6 Sand Washing

1.6.1 Surfactant Solutions

For the room temperature washing, the surfactant solutions or wash solutions were prepared by adding 0.25 g of surfactant to a 50 mL volumetric flask. Deionized water was added to achieve a total mass of 50 g. If necessary, the solution was sonicated to accelerate the dissolution of the surfactant. However, for SAS1, the solution preparation method was slightly different: 0.25 g of the octyl-4-hydroxy-3-nitrobenzoate and sodium carbonate (0.84 g) were added to a achieve a 1:8 octyl-4-hydroxy-3-nitrobenzoate : carbonate mole ratio. Deionized water was again added to achieve a total mass of 50 g.

For the washings done at 50 ºC, the deionized water was first heated in a 150 mL beaker in a water bath to 50 ºC, then added to the surfactant. Sonication was not needed to help dissolve the surfactant.

1.6.2 Sand Washings (Room Temperature and 50 ºC)

The sand washing procedure was adapted from Urum et al.[6] All sand washings were done in triplicate. Approximately 5.0 g of the contaminated sand, 10 g of the desired surfactant solution, and a stir bar were placed into a 20 mL vial, which was then capped with a poly(tetrafluoroethylene)-lined lid. The samples were shaken by hand for 20 s, placed in an otherwise empty 150 mL beaker (for support) and then stirred at 470 rpm for 1 h, re-shaken for another 20 s and stirred for another hour. For the washings at 50 ºC, the samples were placed directly into the water bath, which was previously heated to 50 ºC. The samples were left to stand briefly to let the solution settle. Figure S4 illustrates the sand washing process and Figure S5 shows photographs of some of the samples at the start and end of the 2 h washing period.

After the washing was completed, the liquid phase of the wash mixture was decanted into a separate 20 mL vial and the mass was recorded. This initial decanted solution will be referred to as the first decant. The sand was then rinsed with 50 mL of deionized water and the rinses were combined in a 100 mL Wheaton jar and are henceforth referred to as the rinse solution. The rinse solution was analyzed for oil content as described in section 1.7.3.

A small sample of the decant solution was removed for analysis (see section 1.7.2). The vial containing the remainder of the decant was capped with a rubber septum. CO_2 was bubbled into the vial using a syringe needle at a flow rate of 3 to 5 mL min^{-1} for 10 min. A separate syringe needle was used as a vent. After 10 min, the vial was re-capped with a lid and left to settle overnight, after which the aqueous phase was again analyzed for oil content.

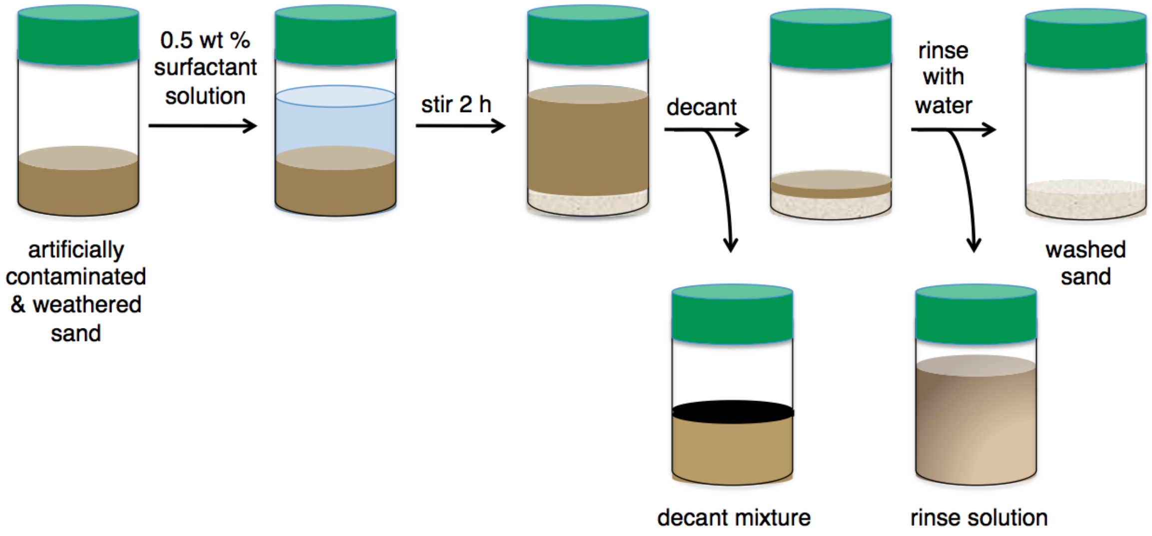
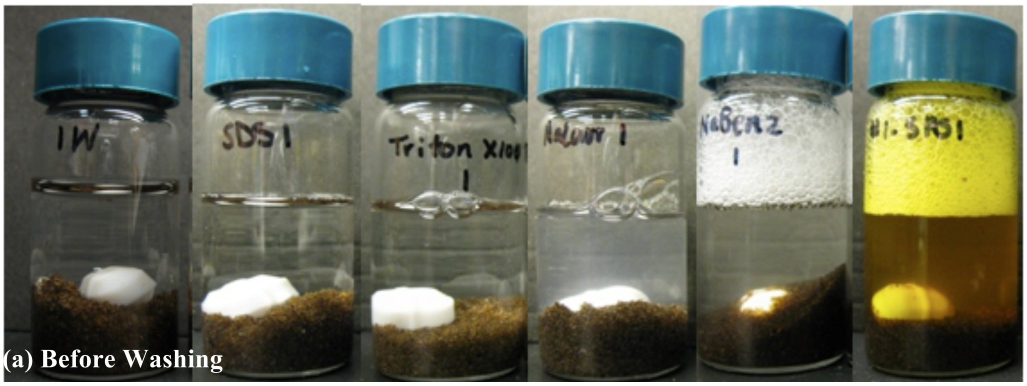


Figure S4. The sand washing process at room temperature.


(a) Before Washing

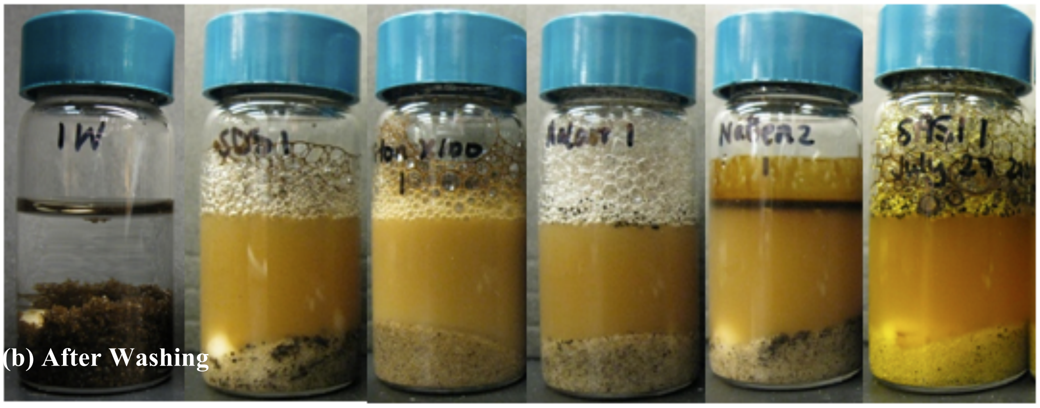

(b) After Washing

Figure S5. Photos of the 23 °C washings (a) at the start and (b) at the completion of the 2 h washing period for (L to R): no surfactant, SDS, Triton X-100, 4a, 3a and 1a.

1.7 Analysis

1.7.1 Analysis of the Oil Content of the Washed Sand

Residual oil remaining on the washed sand was extracted with five 10 mL aliquots of 1:1 v:v dichloromethane:hexanes mixed solvent. The first two aliquots were stirred for 20 min, and the following three were stirred for only 10 min. All extractions were combined in a pre-weighed 100 mL roundbottom flask. The organic, oil containing layer was transferred out of the vial by pipette, passed through a pipette containing a glass wool plug to remove any solid particles, and into the roundbottom flask. The solvent was then removed by rotary evaporation and the mass of oil was determined gravimetrically.

The effectiveness of each surfactant at removing oil from the contaminated sand was calculated from the amount of residual oil using the following equation.

$$\%\ \text{Removal} = \left(1 - \frac{\text{mass of oil remaining on sand}}{\text{total expected mass of oil}}\right) \text{x } 100\%$$

where

$$\text{Total Expected Mass of Oil} = \text{Wt }\%_{\text{Oil on Sand}} \text{ x Sample Mass}$$

1.7.2 Analysis of the Decanted Wash Mixture

Solid Phase Extraction (SPE) was used to determine the amount of oil present in the decanted wash mixture before and after CO_2 treatment. A 3 mL Supelclean™ ENVI-18 SPE tube was placed on a Supelco Preppy SPE Manifold and conditioned with 4 mL of 2-propanol followed by 5 mL of distilled water. The wash mixture decant was briefly shaken to homogenize the sample. A 2 mL aliquot was taken from the wash mixture using a syringe and added to the SPE tube. The oil was washed through the column using a 80:20 [160 mL : 40 mL] methanol:water solution (aqueous solution). The column was then dried under vacuum for 5 min.

The oil was then eluted from the column with 1:1 v:v dichloromethane:hexanes solvent mixture. The eluent was transferred quantitatively to a pre-weighed 25 mL roundbottom flask. The solvent was removed using rotary evaporation and the mass of oil was determined gravimetrically.

1.7.3 Analysis of the Rinse Solution

Solid Phase Extraction (SPE) was used to determine the amount of oil present in the rinse solution. A 20 mL Supelclean™ ENVI-18 SPE tube was placed on a Supelco Preppy SPE Manifold and conditioned with 24 mL of 2-propanol followed by 30 mL of distilled water. The rinse solution in a Wheaton jar was briefly shaken to homogenize the sample and was then passed through the SPE tube. The jar was then rinsed with the 1:1 v:v dichloromethane:hexanes solvent mixture to collect any oil remaining on the walls of the jar. Magnesium sulfate was added to that solvent mixture to remove any residual water. This solution was then added to the SPE tube during the elution of the oil. A final rinse of the tube was done with more 1:1 v:v dichloromethane:hexanes mixture. The eluent was transferred quantitatively to a pre-weighed 100 mL roundbottom flask. The solvent was removed using rotary evaporation and the mass of oil was determined gravimetrically.

2 References

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