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Sugar based amphiphiles: easily accessible and efficient crude oil spill thickening agents†

Malick Samateh^{a,b}, Adiyala Vidyasagar^a, Swapnil R. Jadhav^a, and George John^{a,b}

^aDepartment of Chemistry and Biochemistry & Center for Discovery and Innovation (CDI), The City College of New York, New York, NY 10031, USA

^bPh.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, NY 10016, USA

Abstract

In this work, we demonstrate the use of biomass for the catalytic production of phase-selective gelators (PSGs) as a cost-effective, environmentally benign and ideal method for crude oil spill remediation, as well as execute the study exclusively in crude oil. The use of PSGs has recently provided great promise relative to that of their traditional counterparts. However, the use of PSGs with crude oil is much more complicated due to its complex composition. All of the current PSG methods are demonstrated with refined oils or do not employ eco-friendly methods like enzymatic synthesis. Our current project entails studying sugar alcohol-derived amphiphiles for their phase-selective gelation in crude oil; the PSGs are derived from renewable, benign materials and synthesized *via* a simple, single-step, enzymatic catalysis that required no purification. The results showed that, after a rigorous and systematic testing, the mannitol-derived amphiphile using 8-carbon alkyl chain length (M-8) turned out to be the best crude oil PSG among the studied amphiphiles. M-8 demonstrated a versatility towards thickening of different crude oil types, an efficient ability towards selective gelation of the oil (forming crude oil gel that is over sixty-one-times its mass and stable up to 109.7 °C) in a crude oil/water mixture, and an ability to form gel under practical situations such as seawater conditions. These qualities, in addition to the use of a simple and environmentally benign method to synthesize the structuring agents, make this amphiphile very practical in real life application.

Introduction

One of the most debilitating environmental pollutants that negatively impact the aquatic/marine ecosystem is crude oil spill stemming from several factors such as accidents during drilling or transporting the oil, leakages from oil wells, or volcanic eruption from the sea bed. Examples of the largest crude oil spills in history are the 1989 Exxon Valdez¹ and 2010 BP Gulf of Mexico^{2,3} oil spills, which released about 40 and 210 million gallons of crude oil, respectively, into the sea and environment. The main causes of concern include the loss of a valuable commodity (a non-renewable one), impairment of the ecosystem, and offset of

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Correspondence to: George John.

the climate.⁴ For instance, such devastations were realized in the Exxon Valdez oil spill wherein about 250 000 sea birds, 22 killer whales, 2800 sea otters, 300 harbor seals and vast amounts of fish eggs were killed or destroyed.^{1–3,5–7} Due to the adverse consequences of the oil spills that have tainted our recent history,^{1,5,7} the quest for an effective oil spill remediation has always received special attention. However, remediation methods such as the use of booms, skimmers, high-pressure hot water, burning, and polymeric materials like dispersants, absorbents and solidifiers^{8–10} have notable limitations despite their merits. For instance, booms do not necessarily remove the oil, high-pressure hot water disrupts the microbial populations, burning may be impossible in bad weathers or when too close to the shoreline, and polymeric solidifiers are generally derived from non-renewable resources and difficult in terms of recovering the crude oil from the resulting gel.^{11,12}

Other methods include the use of mechanical pumps and phase-selective gelators (PSGs). Pumps are used to directly extract the oil and an example of such a method has been reported by Ge *et al.*,¹³ wherein a pump is connected to a hydrophobic polymer sponge that sits on and sucks the spilled oil. The limitations of this method include the utility of a whole setup or machinery and polymers which are usually obtained from fossil fuels at a time when efforts are being geared towards curbing the use of non-renewable resources. The use of PSGs has recently shown great promise, with its mode of application slowly but surely evolving.^{14–20} They are used to preferentially solidify the oil which is easily scooped off subsequently. Initially, the method was demonstrated by heating and then cooling the mixture of gelator, oil and water to induce the gelation of the oil phase. Due to the impracticality of heating, dissolving the gelator in a water-miscible solvent for its introduction into the oil phase was adapted and demonstrated.¹¹ Concerns about the intoxication of the aquatic ecosystem by the solvent has been addressed by the use of lipophilic solvent as a vehicle for the gelator.⁴ Further improvement has been recently illustrated by the simple and direct addition of the gelator in the solid form to afford the phase-selective gelation of the oil phase in the mixture of oil and water.²¹

However, oil spills involving crude oil are much more complicated in comparison to their refined oil counterparts like diesel and gasoline by virtue of their highly complex composition.^{22–26} Despite the inevitable merits of phase-selective remediation methods, most of current remediation methods are demonstrated with refined oils like diesel and petrol; direct crude oil remediation methods are very scarce. Additionally, to the best of our knowledge there is no crude oil remediation method that employs eco-friendly methods like enzymatic synthesis.

Continuing our interest in phase-selective gelation as a means of oil spill remediation,¹¹ we herein report studying a range of sugar–alcohol derived amphiphiles for phase-selective behavior in crude oil spill remediation exclusively (Fig. 1). The PSGs are derived from renewable, benign materials and synthesized *via* a simple, single-step, enzymatic catalysis that required no purification.^{27–32} To test the versatility of the PSGs towards crude oil thickening, a wide range of crude oil types with different compositions were chosen for the study. In addition to the simplicity, regiospecificity, and environmentally benign synthesis, the use of sugar alcohols and fatty acids provides leverage for diversity in terms of both starting materials and functionalization, as well as the tunability of property through rational

design. Additionally, the PSGs were tested for their ability to selectively thicken the oil layer while being applied *via* a lipophilic carrier as demonstrated by others.⁴ This was done by preparing a saturated solution of the PSG, which was then added onto the crude oil/water mixture as depicted in Fig. 1b(2).

Experimental section

Materials and methods

Three crude oil types with distinctly different properties were used for this study. The crude oils include Prudhoe Bay Crude Oil (PBCO), Arabian Light Crude Oil (ALCO) and South Louisiana Crude Oil (SLCO). The sugars D-mannitol, D-sorbitol and D-galactitol were obtained from Acros Organics (New Jersey). D-Xylitol was obtained from MP Biomedicals, Inc. (Ohio). The vinyl esters were obtained from Acros Organics. Unless otherwise stated, all solvents and reagents for the synthesis, thin layer chromatography (TLC), work-up and purification were of ACS grade and purchased from Acros, TCI or Spectrum Chemicals Ltd. The TLC plates (silica coated aluminum foil) and silica gel (100–200 mesh) were obtained from Fisher Scientific. The enzyme Novozyme 435 was obtained from Novozymes (U.S.A.). The ¹H and ¹³C-NMR recordings were made using the Varian Mercury 300 MHz NMR Spectrometer, operating at 300 and 75 MHz for ¹H and ¹³C-NMR respectively.

General method for enzymatic synthesis of amphiphiles

The open chain sugar-based amphiphiles were synthesized by enzymatic synthesis. Novozyme 435 was added to a mixture of the sugar alcohol and vinyl esters in dry acetone. The reaction mixtures were shaken at 250 rpm in an incubator shaker, maintained at 50 °C for 48 h. After the incubation, the reaction mixtures were filtered and the solvent removed in rotary evaporator. The dried crude solid products were purified by precipitating in and washing with hexane. All the amphiphiles were obtained as white solids. Furthermore, the reusability of the enzyme was investigated by successively reusing the enzyme to synthesize fresh batches of amphiphile. The usage was repeated until the enzymatic activity was significantly reduced.

(2R,3R,4R,5R)-2,3,4,5-Tetrahydroxyhexane-1,6-diyl dibutyrate, 5a (M-4)—¹H NMR (300 MHz, DMSO-d₆) δ ppm 4. (d, *J* = 5.9 Hz, 2H); 4.31 (m, 4H); 3.96 (m, 2H); 3.60 (m, 4H); 2.28 (t, *J* = 7.3 Hz, 4H); 1.25 (m, 4H); 0.86 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (75 MHz, DMSO-d₆) δ ppm 173.0, 69.0, 68.1, 66.8, 35.5, 18.0, 13.6.

(2R,3R,4R,5R)-2,3,4,5-Tetrahydroxyhexane-1,6-diyl dioctanoate, 5b (M-8)—¹H NMR (300 MHz, DMSO-d₆) δ ppm 4.78 (d, *J* = 5.8 Hz); 4.29 (m); 3.96 (m); 3.58 (m); 2.29 (t, *J* = 7.2 Hz); 1.53 (m); 1.25 (m); 0.86 (m). ¹³C NMR (75 MHz, DMSO) δ = 173.14, 69.82, 67.96, 67.24, 35.10, 33.59, 31.17, 29.72, 24.49, 22.09, 13.35.

(2R,3R,4R,5R)-2,3,4,5-Tetrahydroxyhexane-1,6-diyl bis(decanoate), 5c (M-10)—¹H NMR (300 MHz, DMSO-d₆) δ = 4.80 (d, *J* = 5.9 Hz, 2H); 4.30 (m, 4H); 3.95 (m, 2H); 3.58 (m, 4H); 2.29 (t, *J* = 7.4 Hz, 4H); 1.52 (m, 4H); 1.24 (m, 24H); 0.85 (m, 6H). ¹³C

NMR (75 MHz, DMSO) δ = 173.79, 69.90, 68.73, 67.52, 34.25, 31.98, 29.37, 25.15, 22.79, 14.75.

(2R,3R,4R,5R)-2,3,4,5-Tetrahydroxyhexane-1,6-diyl didodecanoate, 5d (M-12)

^1H NMR (300 MHz, DMSO- d_6) δ = 4.79 (d, J = 5.9 Hz, 2H); 4.30 (m, 4H); 3.97 (m, 2H); 3.70 (m, 4H); 2.28 (t, J = 7.3 Hz, 4H); 1.52 (m, 4H); 1.24 (m, 32H); 0.85 (t, J = 6.5 Hz, 6H). ^{13}C NMR (75 MHz, DMSO) δ = 173.78, 69.77, 68.95, 67.51, 34.26, 29.21, 25.15, 22.54, 15.16.

(2R,3R,4R,5R)-2,3,4,5-Tetrahydroxyhexane-1,6-diyl ditetradecanoate, 5e (M-14)

^1H NMR (300 MHz, DMSO- d_6) δ = 4.71 (d, J = 5.9 Hz, 2H); 4.27 (m, 4H); 4.01 (m, 2H); 3.60 (m, 4H); 2.29 (t, J = 7.3 Hz, 4H); 1.54 (m, 4H); 1.25 (m, 40H); 0.86 (m, 6H). ^{13}C NMR (75 MHz, DMSO) δ = 172.86, 69.23, 68.50, 66.54, 33.49, 31.09, 28.80, 28.52, 24.30, 21.85, 13.64.

(2R,3R,4R,5S)-2,3,4,5-Tetrahydroxyhexane-1,6-diyl dioctanoate, 6b (S-8)

^1H NMR (300 MHz, DMSO- d_6) δ = 4.80 (d, J = 5.8 Hz, 2H); 4.29 (m, 4H); 3.96 (m, 2H); 3.58 (m, 4H); 2.29 (t, J = 7.2 Hz, 4H); 1.53 (m, 4H); 1.25 (m, 16H); 0.86 (m, 6H). ^{13}C NMR (75 MHz, DMSO) δ = 173.64, 71.46, 69.57, 66.29, 35.10, 33.59, 31.17, 29.72, 24.49, 18.61, 14.27.

(2R,3R,4S)-2,3,4-Trihydroxypentane-1,5-diyl dioctanoate, 8b (X-8)

^1H NMR (300 MHz, DMSO- d_6) δ = 4.78 (d, J = 5.8 Hz, 2H); 4.29 (m, 3H); 3.96 (m, 2H); 3.58 (m, 3H); 2.29 (t, J = 7.2 Hz, 4H); 1.53 (m, 4H); 1.25 (m, 16H); 0.86 (m, 6H). ^{13}C NMR (75 MHz, DMSO) δ = 173.14, 69.82, 67.96, 67.24, 35.10, 33.59, 31.17, 29.72, 24.49, 22.09, 13.35.

Gelation and phase-selective gelation studies

Gelation was carried out using two methods namely: (i) the single-phase (known as conventional) gelation, whereby the amphiphile was added to crude oil, a single phase, and then heated; and (ii) the phase-selective gelation, whereby the amphiphile was added to a two-phase mixture of crude oil and water by adding the amphiphile and then heating or as a saturated solution of the amphiphile. Besides the number of phases involved, the gelation process for both single-phase and phase-selective gelations followed the similar protocol as illustrated in Fig. 1b.

Gelation—Typically, a 5% (w/v) gel was prepared by placing a specific amount of crude oil, or oil/water mixture in the case of phase-selective gelation, in a vial and to which the gelator was added. The heterogeneous system was heated to afford a homogeneous dispersion which was allowed to cool slowly to room temperature and then visually observed for gelation.

Minimum gelation concentration—The minimum gelation concentration (MGC) of a gelator was determined by progressively decreasing its % w/v by adding small volume increments of the crude oil (or of both crude oil and water in the case of phase-selective gelation) and then subjecting the new mixture to the gelation procedure described above.

The process was repeated through several cycles until gelation ceased to occur. The maximum amount of solvent immobilized by the given amount of gelator was used to calculate the MGC.

Gel-to-sol-transition temperature—The gel melting temperature, commonly known in the literature as the gel-to-soltransition temperature (T_g), was determined by the typical tube inversion method.^{11,33} In a 2 mL scintillation vial, a 5% w/v gel was prepared as described above. The vial containing the gel was inverted upside down and completely submerged in an oil-bath equipped with a thermometer and slowly heated. The temperature at which the viscous gel melted down was recorded as T_g .

Salt water effect—Furthermore, the effect of seawater on the phase-selective gelation was studied. The seawater was reconstituted by dissolving sea salt in deionized water to obtain 3.5% salt solution. The seawater/PBCO/gelator mixture was heated, allowed to settle for few minutes and then observed for gelation.

Rheology—Rheological studies were performed to discern how the coagulated crude oil would hold and withstand the rigorous action of being scooped out of the mixture containing water. Initially, the linear viscosity region (LVR) was determined *via* strain sweep while keeping the frequency constant at 1 Hz, and then frequency sweep was carried out while keeping the strain rate at a constant value in LVR.

Results and discussion

Most of the current phase selective gelators are synthesized using methodologies that involve multiple steps. From a practical point of view, this results in not only being cost ineffective, but also increases the risk of toxicity exposure for individuals during the process of synthesis, and to the environment during and after disposal. We carried out the synthesis of the PSGs using known enzymatic procedure and different sugar alcohols like mannitol, sorbitol, xylitol and galactitol (Fig. 1a); hence, the building blocks are renewable, biocompatible and degradable, and cost-effective. The enzymatic catalysis renders the procedure simple, single-step, and regiospecific, without requiring purification.

Enzymatic synthesis of amphiphiles

As Table 1 shows, the yields of the enzymatic catalysis range from moderate to good for the distinctly different starting materials. The caprylic acid derivatives of mannitol and sorbitol gave good yield of 93% and 89%, respectively, whereas the other alkyl chain derivatives gave lower yield; xylitol gave relatively poor yield and galactitol did not react at all to form the product. The differences in yield observed may be due to the differences in solubility of different sugars and vinyl esters in acetone, the reaction medium. Thus, the six membered alditols, Mannitol and sorbitol, seem to be more compatible with the reaction medium than the five membered alditol, xylitol. Also, the observed trend in yields seems to suggest that an eight-carbon alkyl chain vinyl ester is more compatible with the reaction medium, resulting in the yields dropping as the number of carbons decreases or increases beyond eight. The information on this dependency of the solubility of the reacting moieties in the reaction medium is very crucial from a practical point of view. In a scenario whereby a particular

amphiphile needs to be commercially produced, a full-fledged optimization of the reaction conditions could be carried out to customize the conditions for the synthesis of the respective sugar-vinyl ester combination.

The lack of reactivity of galactitol under enzymatic conditions to yield the G-8 product is attributed to the chirality of galactitol. The configuration of galactitol is “2*R*,3*S*,4*R*,5*S*” whereas that of the other two six-membered alditols are “2*R*,3*R*,4*R*,5*R*” and “2*R*,3*R*,4*R*,5*S*”, respectively. Potentially, due to the subtle difference in stereochemistry at carbon-3, galactitol may not have effectively interacted with the enzyme as its other six-carbon counterparts. Hence, a configuration of 2*R*, 3*R* and 4*R* may be mandatory for an optimal enzyme–substrate interaction in case of six member alditols.

The investigation of the reusability of the enzyme was studied by employing the same batch of enzyme to synthesize M-8 or S-8 for five times as shown in Fig. 2. The results showed that while using the same batch of enzyme for repeated cycles of M-8 or S-8 syntheses, the yield dropped by less than 18% and 51% during the third and fifth synthesis respectively for M-8; on the other hand, it did by less than 5% and 38% during the third and fifth synthesis respectively for S-8. This ability provides a huge potential for the facile synthesis of amphiphiles in a cost-effective way, which in turn would have a great practical implication for commercial applications.

Gelation studies

Crude oil is a highly complex mixture of hydrocarbons (over 98%) and nonhydrocarbons.²² The hydrocarbons include alkanes, alkenes, cycloalkanes, and aromatic compounds whereas the nonhydrocarbons include nitrogen-, sulfur-, and oxygen-containing compounds as well as metals like nickel, mercury, vanadium and lead. In order to study a wide range of crude oils with different compositional complexity, we used three distinct crude oils namely Prudhoe Bay Crude Oil (PBCO), Arabian Light Crude Oil (ALCO) and South Louisiana Crude Oil (SLCO). Crude oils are generally classified as very light, light, medium and heavy based on API (American Petroleum Institute) values. According to Holder,³⁴ SLCO, ALCO, and PBCO are in the category of very light, light and medium respectively, whereas, according to the American Petroleum Institute,³⁵ PBCO belongs to the heavy category. Additionally, ALCO and PBCO are sour (high sulfur content) while SLCO is sweet (low sulfur content); PBCO is most naphthenic (least paraffinic and most aromatic/naphthenic content) while SLCO is most paraffinic (most paraffinic content) (see Table S2 in the ESI†).^{22–26,34,35}

Single/conventional phase gelation

Alkyl tail dependence of gelation using mannitol-based amphiphiles—derived from vinyl butyrate (M-4), vinyl caprylate (M-8), vinyl caprate (M-10), vinyl laurate (M-12) and vinyl myristate (M-14)—was first studied in the three crude oils through the single phase (also known as conventional) method. The gelation results, shown in Fig. 3a, have indicated that the mannitol-derivatives of the C-8, C-10, C-12 and C-14 alkyl chain lengths underwent gelation in all three crude oil types, whereas C-4, the shortest alkyl chain length, failed to gel in any of the crude oils. Gelation depends on hydrophilic–lipophilic balance (HLB). In crude

oil, a lipophilic medium, the dominance of the former encourages precipitation while that of the latter encourages dissolution. Hence, unlike its longer alkyl chain length counterparts, the chain length of the C-4 derivative is too short to balance-out hydrophilicity of the head group. Thus, the observed failure of M-4 to gel can be attributed to too much dominance of hydrophilicity.

The C-8, C-10, C-12 and C-14 alkyl chain derivatives were studied for their crude oil thickening efficiency. Minimum gelation concentration (MGC) indicates the minimum amount of a particular gelator required to gel a crude oil; the lower the value the more efficient the gelator is. The MGC values (Fig. 3b) indicate that M-8, the C-8 derivative has the best gelation efficiency compared to the other alkyl chain length derivatives. It has an MGC value of 1.4% w/v in Prudhoe Bay crude oil, which implies M-8 could gel an amount of crude oil up to over seventy-time M-8's weight. Both its longer and shorter chain counterparts proved to be poorer gelators; while the longer ones have higher MGC values, the shorter one, M-4, did not gel at all. This observation implies that, on one hand, as chain length increases the solvent–amphiphile interaction gets strong, which weakens the amphiphile–amphiphile interaction; on the other hand, as the chain length gets shorter the amphiphile–amphiphile interaction gets stronger, which weakens the solvent–amphiphile interaction. Solubilization is favored by the former and crystallization by the latter, either of which disfavors gelation. Hence, a proper balance between hydrophobicity (alkyl chain length) and hydrophilicity (hydroxyl group number) gives perfect gelation, which requires the maintenance of amphiphile–amphiphile interaction and solvent–amphiphile interaction optimum.

The gel-to-sol transition temperature (T_g) indicates the thermal stability of the resulting gel. In consistence with MGC results, M-8 turns out to be the best in terms of thermal stability when compared with the other alkyl length derivatives of mannitol. As indicated in Fig. 3c, it has the highest T_g value among all the different alkyl chain derivatives of mannitol; it can withstand high temperatures up to 123.5 °C before its gel reverts to the solution state.

Sugar head group dependence of gelation using eight-carbon-based amphiphiles—derived from the sugars mannitol (M-8), sorbitol (S-8) and xylitol (X-8)—was next studied in the three crude oils *via* the single phase method. As shown in Fig. 4a, the sugar-head-group dependence studies revealed that both M-8 and S-8 underwent gelation in all three crude oils, whereas X-8 failed to gel in any of the oils. This can be attributed to the fact that xylitol has one carbon and one hydroxyl group less compared to the six-membered aldols. As a result, the xylitol's head groups interacted less favorably *via* hydrogen bonding to form an ideal 3D matrix.

The mannitol and sorbitol head group derivatives were compared for their crude oil thickening efficiency. The MGC values shown in Fig. 4b indicated that M-8 is a more efficient gelator in all three crude oils than its sorbitol counterpart. Both mannitol and sorbitol have the same molecular formula but with different chirality at one of the stereogenic centers. Mannitol is (2*R*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol, whereas sorbitol is (2*R*,3*R*,4*R*,5*S*)-hexane-1,2,3,4,5,6-hexol. This subtle difference resulted in a more favorable and cooperative hydrogen bonding interaction for the mannitol head groups than

for the sorbitol head groups. Hence, the mannitol derivative self-assembles into a stronger 3D network than that formed by the sorbitol derivative.

The T_g values for 5% (w/v) gels, shown in Fig. 4c, indicate the mannitol derivative (111.5 to 123.5 °C) to be more efficient in terms of thermal stability in all three crude oils than the sorbitol counterpart (67.2 to 74.3 °C). This observed result is attributed to the same reasoning as mentioned in the case of MGC.

Phase-selective gelation

Phase-selective gelation study in a mixture of crude oil and water was carried out using amphiphiles with the optimal combination of sugar head group and alkyl chain length, M-8 and S-8, determined from the single phase gelation study. The two amphiphiles were investigated for their phase-selective gelation capability, gelation efficiency, thermal stability, and influence of selected oceanic conditions.

As illustrated by the pictures shown in Fig. 5, M-8 and S-8 exhibited phase-selective gelation ability. Fig. 6 shows the results of their phase-selective ability, which is comparable to that of single phase gelation; thus, M-8 and S-8 have demonstrated to be PSGs rather than being mere gelators. Fig. 6a shows both to be capable of forming gels. Fig. 6b and c give the MGC and T_g values comparable to those seen during conventional single phase gelation. M-8 gave the best results, 1.6% w/v for MGC and 109.7 °C for T_g . These results imply that the best PSG, M-8, could gel an amount of crude oil up to over sixty-one-times the weight of the PSG and can withstand high temperatures up to 109.7 °C before the gel ruptures and reverts to the solution form. The T_g value of the phase-selective-selection (109.7 °C) could possibly be close to that of the single phase gelation (123.5 °C) without the additional weight of water above the crude oil gel while inverted during T_g measurement.

To discern how some oceanic conditions might affect the process of self-assembly of the amphiphiles during phase-selective crude oil thickening in a real life scenario, the effect of seawater was conceptually created and tested. Phase-selective gelation using a mixture of seawater (prepared)³⁶ and PBCO was attempted multiple times, with each trial resulting in the crude oil phase being preferentially gelled with M-8 at 5% (w/v). This further strengthens the applicability of these PSGs for practical crude oil spill remediation in the harsh environmental conditions like saltness.

We have also conceptually demonstrated that the sugaralcohol based amphiphile could be applied as a hydrophobic solution to the crude oil spill. A heated saturated solution of M-8 in diesel was added to a crude oil (SLCO)/water mixture (to afford a PSG-in-oil concentration of about 5% w/v), which resulted into the thickening of oil over the water surface as illustrated Fig. 7 (see Video S1 in the ESI†). The result showed the thickened crude oil was coherent and sturdy enough to be scooped out of the water, further making the prospects of practical application more feasible.

The mechanical strength of thickened crude oil was investigated using rheological experiments. Frequency and amplitude dependent experiments were conducted using 5% w/v crude oil gels as shown in Fig. 8 in order to discern the robustness of the coagulated

crude oil and how it would withstand the rigorous action of being scooped out of the water. In rheology, storage modulus (G') gives a measure of the elasticity of a material whereas the loss modulus (G'') gives a measure of the flow behavior (viscosity) of the material under stress. Generally, G' being greater than G'' is characteristic of a stable gel (more solid-like state) and *vice versa* is the characteristic of a sol state. Fig. 8a shows the oscillatory stress response of a 5% thickened M-8 in crude oil. This was carried out by varying strain over a range of % strain values 10^{-3} to $10^2\%$ at a constant frequency of 1 Hz (see Fig. S15 in the ESI†). Both the storage and loss moduli remain fairly constant at about 4000 Pa and 1000 Pa, respectively, over % strain values 0.001–0.01%, the region known as the linear viscosity region (LVR). The gel breaks only at a % strain value of 7.87% (Fig. S15 in the ESI†) or a yield stress value of about 20 Pa (Fig. 8a), characterized by the crossing over of G' and G'' . This result indicates the stiffness of the crude oil gel or the amount of stress to induce strain or deformation, implies the thickened crude oil to be stable as a gel, and indicates good tolerance to external stress.

Fig. 8b shows a typical frequency sweep experiment whereby the variation of G' and G'' was monitored as a function of applied frequency under a constant strain 0.01%. For the crude oil gel under study, G' (about 6000 Pa) was found to be higher than G'' (about 1500 Pa) and they did not cross each other throughout the experimental region (0.01 to 10 Hz). This result suggests the formation of viscoelastic material capable of tolerating the scooping action of the gel out of the water in a practical scenario.

Conclusions

In conclusion, this work has demonstrated an economical and environmentally friendly means of generating PSGs for oil spill remediation exclusively in crude oil. After systematic and rigorous testing and screening, M-8 and S-8 have emerged as the best sugar alcohol-based amphiphiles for crude oil spill remediation. The PSGs exhibited great versatility towards crude oil thickening by gelling different crude oil types that have contrasting properties. M-8 selectively thickened crude oil in a crude oil/water mixture; efficiently gelled a mass of crude oil over sixty-one-times its mass; and yielded a thermally stable gel up to 109.7 °C. The ability of M-8 to withstand strong ionic strength, which is some reality found in aquatic environments where crude oil spills commonly occur, is indicative of the effectiveness in practical and real-life applications. Furthermore, M-8 has proven to be capable being introduced into the crude oil phase as a solution using a lipophilic solvent as a carrier. Thus, this study has conceptually shown that the sugar-based PSGs are ideal contenders for crude oil-spill remediation due to being derived from renewable, ecofriendly, and low-cost resources; synthesized *via* a simple, single-step, enzymatic catalysis that required no purification; and studied exclusively in different crude oils. The low cost of these least explored sugar alcohols and the potential recyclability of the enzyme and reaction medium would inevitably make the herein proposed crude oil spill remediation cost effective in comparison to the existing mitigation strategies.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Schematic illustration of synthesis and gelation. (a) Enzymatic synthesis of amphiphiles using open-chain sugar alcohols. (b) Phase-selective gelation of crude oil *via* both the addition of solid powder and then heating (b-1), and addition of gelator solution (b-2).

Fig. 2.
Percent yield with repeated enzyme use for synthesizing different batches of M-8, (a); and S-8, (b).

a)

Crude Oil	M-4	M-8	M-10	M-12	M-14
PBCO	N/A	G	G	G	G
ALCO	N/A	G	G	G	G
SLCO	N/A	G	G	G	G

G = gelation occurred.

N/A = no gelation; remained solubilized or precipitated out.

b)

c)

Fig. 3.

Results of alkyl chain length dependence of: (a) gelation; (b) MGC value; and (c) T_g value.

a)

Crude Oil	M-8	S-8	X-8
PBCO	G	G	N/A
ALCO	G	G	N/A
SLCO	G	G	N/A

G = gelation occurred.
N/A = no gelation; remained solubilized or precipitated out.

Fig. 4.
Results of head group dependence of: (a) gelation; (b) MGC value; and (c) T_g value.

Fig. 5.

Representative picture of a typical gel formed *via* phase-selective gelation: (a) a tilted vial containing crude oil gel alongside that containing liquid crude oil – the level of the gel is not perpendicular to the direction of pull of gravity while that of the liquid is observed to be so; (b) verification of crude oil gel formation by inverting the vial upside down.

a)

Crude Oil	M-8	S-8
PBCO	G	G
ALCO	G	G
SLCO	G	G

G = gelation occurred.

b)

c)

Fig. 6.

The phase-selective gelation results for: (a) gelation; (b) MGC value; and (c) T_g value.

Fig. 7. Snapshots from crude oil gelation using a heated solution of M-8 in diesel: (a) clear water prior to crude oil addition; (b) addition of crude oil (SLCO) to water; (c) addition of a molten solution of M-8 in diesel; (d) removal of the gelled crude oil after about 90 seconds; (e) the scooped crude oil gel; and (f) cleaned-up water.

Fig. 8.
Rheology data of 5% M-8 in crude oil (SLCO). (a) Stress amplitude sweep and (b) frequency sweep.

Table 1
Yields, compound #'s, and abbreviations assigned to the synthesized amphiphiles^a

Serial #	Sugar	R	Compound #	Abbr.	% yield
1	Mannitol	COC ₃ H ₇	5a	M-4	39.0
2		COC ₇ H ₁₅	5b	M-8	93.0
3		COC ₉ H ₁₉	5c	M-10	87.3
4		COC ₁₁ H ₂₃	5d	M-12	87.3
5		COC ₁₃ H ₂₇	5e	M-14	62.4
6	Sorbitol	COC ₇ H ₁₅	6b	S-8	88.9
7	Galactitol	COC ₇ H ₁₅	7b	G-8	N/A
8	Xylitol	COC ₇ H ₁₅	8b	X-8	53.0

^a All reactions were carried out at 50 °C for 48 hours.

Abbr. = abbreviation. N/A = no product obtained.