Phase-Selective Sorbent Xerogels as Reclamation Agents for Oil Spills

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ABSTRACT: 12-Hydroxystearic acid (12-HSA) xerogels derived from 12-HSA–acetonitrile organogels are highly effective sorbent materials capable of adsorbing apolar, spilled materials in aqueous environments. 12-HSA xerogels made from 12-HSA–acetonitrile organogels are more effective than 12-HSA xerogels made from 12-HSA–pentane organogels because of the highly branched fibrillar networks established in acetonitrile molecular gels. This difference arises because of dissimilarities in the network structure between 12-HSA in various solvents. These xerogels, being thermoreversible, allow for both the spilled oil to be reclaimed but also the gelator may be reused to engineer new xerogels for oil spill containment and cleanup.

INTRODUCTION

Waterways facilitate the transport of the world’s petrochemical supply; however, there are associated risks with this mode of transport, as witnessed by the over 30 significant oil spills (i.e., >7000 tons of crude oil released per incident) since 2000.1 Confounding the issue, underwater exploration and offshore drilling increase the risks of petrochemicals entering our waterways. In 2010, nearly 5 billion barrels of crude oil were released in the Gulf of Mexico.2 Each incident has a devastating effect on Earth’s delicate ecosystems. The presence of both crude oil and the chemical dispersants, used to disperse the oil, can disrupt sensitive food webs and create situations of toxin bioaccumulation.

Current materials used to clean spilled oil are subdivided into three primary categories, including dispersants, sorbents, and solidifiers.3 Dispersants emulsify the oil into small finely divided droplets and disperse them in the environment.3,5 Sorbents are typically powders that selectively absorb the oil via capillary forces within a superhydrophobic matrix.6–8 Solidifiers gel the material on the surface of the water using either polymeric or monomeric gelators.3,9,10 Ideally, any material used to treat spilled oil in our waterways must selectively remove the oil phase from water, be nontoxic, and allow oil to be reclaimed, and the material should be recyclable or reusable.3 A recent surge in interest using amphiphilic molecular gelators to solidify spilled oil includes sugar alcohols,3 amino acid amphiphiles,11 aromatic amino acids,9 and modified 12-hydroxy-N-alkylocta-decanamide.10 A different, novel approach to remove spilled oil from water is to use a xerogel, which will adsorb the oil from the water. The separation ability of a xerogel arises from the hydrophobicity of the gelator, while the driving force of adsorption is the capillary forces arising from the void volumes within the xerogel created by the fibrillar aggregates. Hence, the ability to form a highly porous xerogel, using the simplest method, is central to developing a low-cost sorbent-based xerogel to be used as an oil reclamation agent.

MATERIALS AND METHODS

Organogel and Xerogel Preparation. The samples were prepared in 10 mL vials by adding 0.125 g of 12-hydroxystearic acid (12-HSA) to 5 g of the organic solvent. Solvents were selected on the basis of their ability to be gelled by 12-HSA and their high volatility at atmospheric pressure. The three organic solvents tested were acetonitrile, pentane, and diethyl ether. Each of the vials were capped and heated to 80 °C for 20 min to allow for 12-HSA to dissolve into the solvent. The sols were cooled and stored at 25 °C for 24 h, allowing the gel to form. After organogelation, the vials were uncapped under atmospheric pressure for at least 24 h, allowing for the solvent to evaporate from the organogel, leaving behind the xerogel. Samples were stored below the melting point (~60 and 65 °C) of the xerogel in an incubator set at 40 °C.

Oil Spill Simulation. Two different setups were used to simulate the oil spill. The first setup used 10 mL beakers each containing 3 g of distilled water and 3 g of 10W-40 motor oil. The second setup used 3 g of sterile seawater (Sigma-Aldrich, lot 070K8431) and 3 g of diesel fuel (Exxon Mobile) or 3 g of regular gasoline (87 octane, Exxon Mobile). The mass of the oil/fuel, water, and beaker system was then weighed and recorded. A known amount of xerogel was placed onto the top of a simulated oil spill and left quiescent for 1 h, after which time the sample was removed and blotted dry using Kimwipes to remove residual surface oil. To obtain the kinetics of adsorption, gels were removed from the beaker and the weight of the gels was recorded every min for the first 5 min, every 5 min from 5 to 30 min, and then every 15 min from 30 min to 1 h for the 10W-40 motor oil in distilled water. From these data, the mass of the oil absorbed from the different gels could be calculated, and the information was used to calculate the percent of oil absorbed with respect to the mass of the xerogel. A second set of experiments determined the amount of diesel or gasoline adsorbed by the gel from seawater after 60 min and is presented as a percent weight change of the xerogel.

Microscopy. Brightfield micrographs were obtained by placing the sample onto a 25 × 75 × 1 mm glass slide, and a coverslip was applied to the sample (Fisher Scientific, Pittsburgh, PA) after being heated to...
Samples were imaged on a Linkham microscope (Linkham Scientific Instruments, Surrey, U.K.) with a 10× objective lens (N.A. 0.25). A charge-coupled device (CCD) color camera (Olympus, Center Valley, PA) acquired images as uncompressed 8-bit (256 gray-scale) TIFF files with a 1280 × 1024 spatial resolution.

X-ray Diffraction (XRD). The XRD or wide-angle X-ray scattering (WAXS) patterns of 12-HSA gels in different solvents were obtained by use of a Bruker HiStar area detector and an Enraf-Nonius FR571 rotating anode X-ray generator equipped with a Rigaku Osmic mirror optic system (~0.06° 2θ nominal dispersion for Cu Kα; l = 1.5418 Å) operating at 40 kV and 40 mA. All of the data were collected at room temperature over a period of about 300 s. The sample–detector distance was 10.0 cm, and the standard spatial calibration was performed at that distance. Scans were 4° wide in ω with a fixed detector or Bragg angle (2θ) of 0° and fixed platform (f and c) angles of 0° and 45°, respectively. In all cases, the count rate for the area detector did not exceed 100 000 counts per second (cps).

Rheology. An AR-G2 hybrid rheometer (TA Instruments, New Castle, DE) was used to probe the macroscopic properties of the gels. An 8 mm flat, serrated, parallel plate (TA Instruments, New Castle, DE) was used to carry out the oscillatory measurements. Small deformation oscillatory rheology was employed to determine the complexes $G'$ and $G''$ within the linear viscoelastic region (LVR) of the gel at 1 Hz by carrying out a stress sweep at 10−500 Pa.

RESULTS AND DISCUSSION

Numerous solvents are structured into organogels when 12-HSA, a hydrogenated component of castor seed oil, is added in low concentrations.12 The hydrogenated derivative of castor seed oil is enantiomerically pure, which allows for gelation at much lower concentrations.13 Dependent upon the solvent, the critical gelation concentration (CGC) varies between 0.5% for alkanes (i.e., pentane, hexane, etc.) and 2.3% for nitriles (i.e., ethyl nitrile and butyl nitrile).12 The difference in the CGC between alkanes and nitriles pertains to the polymorphic form of the molecular gel. In alkanes, a hexagonal subcell spacing (~4.1 Å) and a multilamellar crystal morphology, with a distance between lamella greater than the bimolecular length of 12-HSA, corresponded to molecular gels with the CGC less than 1 wt % (Figure 1A).14 12-HSA molecular gels in nitriles have a much higher CGC corresponding to a triclinic parallel subcell (~4.6, 3.9, and 3.8 Å) and interdigitation in the lamella (Figure 1B).

Upon cooling the sol, gelator molecules phase-separate and interact via non-covalent interactions; in the case of 12-HSA, dimerization occurs between the carboxylic acid groups and longitudinal growth is promoted by the hydroxyl group at position 12, forming hydrogen bonds between adjacent 12-HSA molecules (Figure 2).15−19 SAFiNs, in organic solvents, require a meticulous balance between contrasting parameters, including solubility and those intermolecular forces that control epixial growth into axially symmetric elongated aggregates.20 The precise ratio of gelator−gelator interactions to gelator−solvent interactions is established to play a central role in the formation of an organogel and the length of the fibrillar aggregates.21−23 12-HSA−acetonitrile molecular gels have a drastically different microstructure than the 12-HSA−pentane microstructure (Figure 3). In acetonitrile, numerous fibers radiate from a central nuclei, forming more numerous, shorter fibers compared to 12-HSA in pentane. The differences in the crystalline structure will give rise to the difference in the number and size of the pores and, hence, the magnitude of the capillary forces. Because the self-assembly process of organo-
gelators requires such an important balance of solvent polarity, water content, and additives to effectively immobilize the continuous phase, our aim is to minimize the impact of the solvent when containing spilled materials. Recently, a group of sugar-derived gelators showed promise to contain oil spills because of their robust ability to form gels in numerous environments.24,25 Our strategy is distinctively different, where the organogel is formed in a very controlled environment and then the solvent is removed, creating a xerogel (Figure 3). Solvents were selected on the basis of their low vapor pressure at atmospheric conditions and ability to form an organogel at low concentrations. Using these criteria, three solvents were selected, pentane, acetonitrile (ethyl nitrile), and diethyl ether. Diethyl ether formed a very fragile xerogel, which was difficult to handle, and, therefore, was not analyzed further. The organogels had a higher elastic modulus than loss modulus (acetonitrile, $G' = 252,940 \pm 14,918 \text{ Pa}$ and $G'' = 43,124 \pm 4,564 \text{ Pa}$; pentane, $G' = 322,000 \pm 19,312 \text{ Pa}$ and $G'' = 51,462 \pm 9,414 \text{ Pa}$) indicating that the materials were gels.

The samples were uncapped and allowed to evaporate for 72 h to ensure that the majority of the solvent had evaporated. Upon evaporation, resulting in the transformation of the organogel to a xerogel, the elastic modulus increased drastically (acetonitrile, $G' = 620,629 \pm 32,829 \text{ Pa}$ and $G'' = 47,107 \pm 5,919 \text{ Pa}$; pentane, $G' = 502,600 \pm 11,142 \text{ Pa}$ and $G'' = 42,662 \pm 4,328 \text{ Pa}$). Dependent upon the solvent volatility, the rate that the gels dried varied greatly and affected the structure of the xerogel. As seen in Figure 4, ethyl nitrile (acetonitrile) had very little collapse in the structure, maintaining a large volume, while pentane and more obviously diethyl ether collapsed into very dense xergels, which can be correlated to the differences in the microstructure and ultimately differences in the nanostructure of the crystalline phase. Each of these systems was placed into the simulated oil spill, and the mass gained after 1 h (Figure 5) was measured to see if the capillary forces were sufficient to draw the hydrophobic solvent into the empty pores of the xergels. The 12-HSA xerogel produced from diethyl ether did not adsorb solvent during the experiment; the xerogel produced using pentane increased its mass by $93 \pm 9.2 \text{ wt \%}$, while the xerogel made from 12-HSA in acetonitrile increased its mass by $387 \pm 21 \text{ wt \%}$ in distilled water and 10W-40 motor oil (Figure 5). To ensure that the mass gained was from motor oil and not water, the 12-HSA xerogel produced using acetonitrile was placed in water. The mass gained after 1 h was $3.85 \pm 0.5 \text{ wt \%}$ in distilled water and $5.23 \pm 1.2 \text{ wt \%}$ in seawater, effectively demonstrating that the xerogel was phase-selective in adsorbing the oil. The 12-HSA xerogel made using acetonitrile as the solvent was also tested on diesel in seawater and regular gasoline in seawater. After exposure for 1 h of the

![Figure 3. Brightfield micrographs of (A) 2.5 wt % 12-HSA–acetonitrile and (B) 2.5 wt % 12-HSA–pentane organogels. The width of the micrograph is 120 μm.](image)

![Figure 4. Organogels produced in three different solvents and the resulting 0.125 g of xergels after 72 h of drying. The simulated oil spill was performed in triplicate for the weight gain after 1 h and the time-resolved adsorption.](image)
xerogel to the simulated spill, the xerogel increased in weight by 459 ± 33 wt % in diesel and 583 ± 42 wt % in gasoline. This illustrates that the 12-HSA xerogel is not only effective but also very versatile in its applications of reclaiming spilled oil. It has previously been shown that similar materials (i.e., silica aerogels) are far less effective (~0.1 wt % gain) than 12-HSA xerogels (~583 wt % gain). However, 12-HSA xergels absorb similar amounts of oil as a Bregoil sponge (made from waste-wood fibers) (weight gain of ~700 wt %), and cellulose fibers (weight gain of 375 wt %). Although, the 12-HSA xerogels do not absorb as much oil as the most advanced materials (i.e., superwetting cryptomelane-type manganese oxide nanowires). 12-HSA xergels are as selective for the apolar phase and are derived from much lower cost castor seed oil.

It is obvious from the weight gained and oil recovered that the xerogels made from 12-HSA and acetonitrile are very effective phase-selective sorbent materials. The major advantage of using the xerogel, as opposed to forming an organogel in the environment, is that this system is not dependent upon environmental factors. As long as the material of interest is apolar, our sorbent xerogel pellets will be an effective mode to contain and remove the materials from the environment.

CONCLUSION

Xerogels formed using 12-HSA and acetonitrile are highly effective sorbent materials capable of adsorbing apolar, spilled materials in aqueous environments. 12-HSA organogels in acetonitrile are more effective at producing xerogels, capable of adsorbing spilled oil, than from pentane because of the highly branched fibrillar networks established in acetonitrile molecular gels. This difference arises because of dissimilarities in the network structure between 12-HSA in various solvents. These xerogels, being thermoreversible, allow for both the spilled oil to be reclaimed but also the gelator may be reused to engineer new xerogels for oil spill containment and cleanup.

REFERENCES


