Supporting Information

Xylitol Based Phase Selective Organogelator for Potential Oil Spillage Recovery

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Material and Methods

Materials

Reagent- or analytical grade chemicals were purchased from Merck-India and used without further modifications. Synthesis grade solvents were purchased from Merck-India and dried according to standard procedures whenever required.

Instruments and Characterization

$^1$H NMR spectra were recorded on JEOL ECZ 500 MHz spectrometer. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a quadruple mass spectrometer (Shimadzu 2020). Elemental analyses were performed on Vario Macro Cube CHNSO analyzer. SEM experiments were performed using a JEOL Scanning Microscope taking the gel over a carbon tape followed by gold coating. FT-IR spectroscopy was performed using Perkin Elmer FT-IR spectrophotometer in ATR mode over diamond crystal.

Microscopy study:

SEM experiments were performed on a Zeiss Scanning Microscope Gemini SEM300 with gold coating. A drop of gel was placed on a piece of cover slip and desiccated for few hours under vacuum before imaging.

Rheological studies:

The rheological experiments were carried out in cone and plate geometry (diameter 40 mm) on the rheometer plate using an Anton Paar MCR 302 rheometer. The gels were scooped on the rheometer plate so that there was no air gap with the cone. Both frequency and oscillatory stress sweep experiment was performed at 25°C.

Experimental Procedure:

Synthesis of Compound 1: Sugar based amphiphiles were synthesized by conventional solution phase methodology following the procedure for Sorbitol based compounds as reported previously. $^1$ Cyclohexane (60 ml) and MeOH (15 ml) was added to a round bottomed flask and
kept under N\textsubscript{2} atmosphere. Xylitol (4.2 g, 27.5 mmol) and p-TsOH (0.5 g, 2.7 mmol) was added to the solvent mixture and heated to 80\textdegree C for 10 min to obtain a clear solution. Benzaldehyde (5.6 ml, 55 mmol) was added to it and refluxed at 80\textdegree C for 2 hours. During refluxing, reaction mixture turned semi solid form which white cake was obtained after solvent evaporation. Unreacted xylitol were removed by water washing of the cake and the product 1 was obtained as white solid after column chromatographic purification using DCM-MeOH as eluent. Yield = 90%. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, rt): \(\delta = 7.60-7.58\) (dd,4H), 7.54-7.52 (t, 2H), 7.41-7.34 (m, 4H), 5.66 (s, 1H), 5.58 (s, 1H), 4.41-4.39 (dd, 1H), 4.16-4.14 (dd, 1H), 4.09-3.97 (m, 3H), 3.86-3.84 (dd, 2H); ESI-MS: m/z: 329.2 [M+H]\textsuperscript{+}, m/z (calculated): 328.1 [M]\textsuperscript{+}; E.A: calculated for C\textsubscript{19}H\textsubscript{20}O\textsubscript{5}: C, 69.50; H, 6.14, Found: C, 69.43; H, 6.21.

Synthesis of Compound 2: Compound 2 was also synthesized following the reaction procedure as that of previous reaction but using acetophenone (3.2 ml, 27.5 mmol) instead of benzaldehyde. The reaction mixture was refluxed for 12 hours. The mixture thus obtained after reaction was subjected to washing by water and the product was obtained in 64% yield as a white solid after purification by column chromatography. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, rt): \(\delta = 7.97-7.95\) (d, 4H), 7.58-7.55 (t, 2H), 7.48-7.46 (t, 4H), 4.42-4.39 (dd, 1H), 4.23-4.21 (dd, 1H), 4.08-3.87 (m, 3H), 3.55-3.53 (dd, 2H), 1.68 (s, 6H); ESI-MS: m/z: 357.2 [M+H]\textsuperscript{+}, m/z (calculated): 356.1 [M]\textsuperscript{+}; E.A: calculated for C\textsubscript{19}H\textsubscript{20}O\textsubscript{5}: C, 70.77; H, 6.79, Found: C, 70.93; H, 6.85.

Synthesis of Compound 3: Compound 3 was synthesized following the reaction procedure as that of compound 1 but using phenyl ethyl ketone (3.7 ml, 27.5 mmol) instead of benzaldehyde. The reaction was performed for 24 hours to obtain semi solid mixture. The mixture thus obtained was washed with water and the product was isolated in 64% yield as a white solid after purification by column chromatography. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, rt): \(\delta = 7.97-7.95\) (d, 4H), 7.57-7.53 (t, 2H), 7.47-7.43 (t, 4H), 4.43-4.41 (dd, 1H), 4.20-4.17 (dd, 1H), 4.05-3.80 (m, 3H), 3.53-3.50 (dd, 2H), 3.03-2.98 (q, 4H), 1.24-1.21 (t, 6H); ESI-MS: m/z: 385.2 [M+H]\textsuperscript{+}, m/z (calculated): 384.1 [M]\textsuperscript{+}; E.A: calculated for C\textsubscript{19}H\textsubscript{20}O\textsubscript{5}: C, 71.85; H, 7.34, Found: C, 71.83; H, 7.21.

**Gelation experiment:**

All of these xylitol based compounds were subjected to gelation experiment for the first time. In a typical procedure, the gelator compound was added to 0.5 ml of oil in a glass vial with an internal diameter (i.d.) of 10 mm. The mixture was warmed gently to dissolve the solid
compound. The solution was then allowed to cool slowly to room temperature without disturbance. After few minutes, the solid aggregate mass was found to be stable to inversion of the glass vial, and then the compound was recognized to form a gel.

Phase selective gelation experiment was performed by dissolving the gelator compound in the biphasic mixture having specific oil of 0.5 mL in presence of 0.5 mL of water. Cooling of the mixture at room temperature resulted oil layer in gel state, keeping the water layer intact in the liquid state.

**Phase selective gelation study and recovery:**
Initially the gelator solution was prepared by dissolving 2.5 g of gelator 1 in 10 ml of toluene (25% solution). This solution was added to a mixture of crude oil/different refinery distillates and water (1 ml toluene solution for 10 ml of crude oil and 0.5 ml toluene solution for 10 ml of diesel) in a glass vial. The mixture was then kept undisturbed. In the course of the process, the il phase was converted to gel in less than a minute, keeping the water phase intact.

For recovery study, 100 mL of individual oil i.e crude oil, SRN, diesel over 5 L of water was taken in glass tray. Required amount of gelator dissolved in toluene was added (using gelator amount more than MGC value i.e. 10 ml 25% toluene solution for 100 ml crude oil/SRN and 5 ml 25% toluene solution for 100 ml diesel). The resulting gel was scooped out, and the oil phase was recovered through vacuum distillation as shown in supporting video for gelation of SRN and its recovery. The oil recovery from gel phase was calculated as 97% for SRN, 95% for diesel and 53% for crude oil (heavy oils from crude were not recovered by vacuum distillation). The boiling point range for recovered oil from crude was monitored by micro distillation (ASTM D7345 method).

Recyclability of gelator 1 was also performed after collecting the oil from gel. As shown in the supporting video, white solid of the gelator compound was collected back after oil recovery. The recovered gelator was again used for oil phase (SRN) uptake. The experimental results showed that after 1\textsuperscript{st} step, uptake capacity decreased to about 97% which also decreased further in the upcoming cycles and exhibited about 90% efficiency after fifth cycle. The reason for this activity drop may be due to the presence of little bit of water in collected gel form biphasic mixture, that may lead to acetal/ketal bond hydrolysis of the gelator at elevated temperature during oil recovery. Recyclability test for crude was not performed but in a different way. After 53% of oil
recovery for crude gel, the unrecovered bottom which consists of heavy oils along with the
gelator remained in gel form after cooling.

**XRD Studies:** Powder XRD studies were performed with X’pert3 X-ray diffractometer from
PANalytical, Netherlands. Source: Cu K-alpha, 0.15418 nm (Bragg-Brentano geometry). Sample
was scanned at 0.25 °/min from 5 to 50 ° with a step size of 0.008. The scan voltage and current
were fixed at 45 kV and 30 mA respectively. The XRD spectrum is given below.

![XRD Spectrum](image)

The XRD pattern of gel with four strong reflections was considered to understand the packing of
molecules. Their corresponding d-spacing and the ratio of d-spacing with respect to $d_1$ is given in below
able. Ratio of d-spacing suggests that the molecules are arranged in layers.

<table>
<thead>
<tr>
<th>2θ (in degrees)</th>
<th>d-spacing (Å)</th>
<th>Ratio of d-spacing with respect to $d_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.150</td>
<td>14.3603 ($d_1$)</td>
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</tr>
<tr>
<td>11.820</td>
<td>7.4814 ($d_2$)</td>
<td>2</td>
</tr>
<tr>
<td>20.921</td>
<td>4.2426 ($d_3$)</td>
<td>3</td>
</tr>
<tr>
<td>23.186</td>
<td>3.8331 ($d_4$)</td>
<td>4</td>
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