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Recovery of fuels using the supramolecular gelation ability of a hydroxybenzoic acid bisamide derivative

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Abstract: In order to remedy the environmental pollution caused by oil spills, new materials with gelation capacity of organic solvents and fuels have been synthesized during the recent years. Among them, some of the most promising materials contain amide groups, which are often incorporated into the chemical structure of organogelators due to their effectiveness in gelling organic solvents through hydrogen bonds. A bisamide derivative of hydroxybenzoic acid (Bis-HUB1) was designed and synthesized in two steps and is able to congeal organic solvents. Gelation tests, critical gelation concentrations and gel-sol transition temperatures were discussed in terms

of its supramolecular interactions. Intermolecular hydrogen bonds and π - π stacking were studied through variable-temperature FTIR and UV-visible spectroscopy, while the structural characterization was performed via freeze-fracture TEM. Interestingly, Bis-HUB1 showed the ability to gel gasoline and diesel from monophasic and biphasic systems, which implies its potential use as a remediation agent in fuel spills. The results encourage further research.

Keywords: organogelator; bisamide; non-covalent interactions; fuel recovery, water pollution

1 Introduction

Some of the most astonishing engineering disasters have outlined the path through which scientific research has been focused in recent years (Murphy et al., 2016). For example, the Deepwater Horizon rig explosion in the early beginning of this decade, and the subsequent spill of 4.9 million barrels of oil in the Gulf of Mexico has been considered as one of the worst long-term environmental disasters of the modern history, because of its affections to both ecosystem equilibrium (Pasparakis et al., 2019; Schwing et al., 2018; Wise et al., 2018) and human health (Fernando et al., 2019; Gam et al., 2018; Laffon et al., 2016).

Due to the necessity of containing and collecting oil from spills, some materials have been studied for this purpose; for instance, dispersants that emulsify the oil, solid powders that absorb it, or solidifiers that are usually polymeric materials that recover the oil by gelling the hydrocarbon layer (Okesola and Smith, 2016). However, since 2001, when a phase-selective low molecular weight organogelator (PSOG) was reported for the first time (Bhattacharya and Krishnan-Ghosh, 2001), the interest of synthesizing new and simple organogelators exhibiting the ability of gelling hydrocarbons has increased owing to their excellent selective gelation properties towards the oil phase, their well-defined molecular structure compared to polymeric materials, the possibility of performing molecular design on the gelator structure to add functionality and improve their affinity, as well as because they provide easy and non-hazardous ways of recovering the oil (Ohsedo, 2016; Raju et al., 2016; Vibhute and Sureshan, 2020).

In this context, the progress of contemporary science and technology lies, to a great extent, on the recent developments and understandings in the field of materials science, where soft materials play a predominant role. At the present time, many conventional materials have been increasingly

displaced by soft materials due to their enhanced properties and their ability to show smart responses to external stimuli, which confers them exceptional performance and broader applications (Liu and Li, 2013). This typical response to subtle changes in their surroundings makes that soft matter, and particularly, organogels, be interesting for both research and industrial purposes.

Organogels are colloidal systems formed essentially by an organic solvent which behaves macroscopically more similar to an elastic solid than to a viscous fluid. Although its main constituent is a liquid, the presence of a self-assembled three-dimensional network of crosslinked solid fibres is responsible for the immobilization of the solvent, which causes that the organogel system exhibit viscoelastic properties (Shakeel et al., 2020).

In this article, a new bisamide organogelator is studied, the 3,5-bis-(11-hexylcarbamoyl-undecanoxy)-benzoic acid methyl ester (Bis-HUB1), which contains an ester group, an aromatic ring and a long alkyl chain, so that in addition to the hydrogen-bonding site provided by the amide groups, the ester may be a source of dipole-dipole interactions, the aromatic ring was adopted to act as a π - π stacking unit, while the alkyl chain served as a hydrophobic building block, which operates in a synergic way affording molecular flexibility for aggregation and self-assembly in organic solvents (Zapién-Castillo et al., 2020).

Besides its gelation tests in organic solvents, the bisamide gelator showed gelation ability of diesel and of two types of gasoline, as well as selective gelation of gasoline from a monophasic system and biphasic water/gasoline mixture, which suggest its potential use as low molecular weight solidifier for oil recovery from spills.

2 Materials and methods

2.1 Materials

11-bromoundecanoic acid (95%), 1-hexanamine (99%), silica gel (high purity grade), 3,5-dihydroxybenzoic acid methyl ester (97%) and tetrabutylammonium bromide (95%) were purchased from Sigma-Aldrich; N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride or EDCI ($\geq 98\%$) and 1-hydroxybenzotriazole or HOBt ($\geq 98\%$) were purchased from Fluka; sodium bicarbonate (99.7%) was purchased from BDH, and hydrochloric acid (37%) was

purchased from Emsure. Dimethylformamide (99.7%), dichloromethane ($\geq 99.5\%$), n-hexane (99%), toluene (99.8%), acetonitrile (99.5%), and chloroform-d (99.8% atom) with tetramethylsilane (1% v/v) were purchased from Sigma-Aldrich; methanol (99.8%), ethanol (99.9%), and cyclohexane (99.9 %) were purchased from Fermont; ethyl acetate ($\geq 99.5\%$) was purchased from J. T. Baker. Additionally, three commercial fuels were used: 87 octane rating gasoline (GM), 92 octane gasoline (GP), and diesel.

2.2 Synthesis of Am-HU and Bis-HUB1

2.2.1 11-bromoundecanoic acid hexylamide (Am-HU)

A solution of nearly equimolar amounts of 11-bromoundecanoic acid (4.81 g, 18.1 mmol) and 1-hexanamine (1.76 g, 17.4 mmol) was prepared in dichloromethane (70 mL) under an inert nitrogen atmosphere, and an excess of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI, 5.06 g, 26.4 mmol) and 1-hydroxybenzotriazole (HOBt, 4.06 g, 30 mmol) were added as coupling agents. The reaction proceeded 2 h at 0 °C and 700 rpm, followed by 48 h at room temperature. The product of the reaction was neutralized using an aqueous solution of sodium bicarbonate (100 mL, 10% w/w), and purified by filtering it through a silica-gel bed using a solution of hexane and ethyl acetate (200 mL, 50% v/v) as carrying phase.

2.2.2 3,5-bis-(11-hexylcarbamoyl-undecanoxy)-benzoic acid methyl ester (Bis-HUB1)

3,5-dihydroxybenzoic acid methyl ester (355 mg, 2.1 mmol), compound Am-HU (1508 mg, 4.3 mmol), potassium carbonate (1459 mg, 10.6 mmol), and tetrabutylammonium bromide (275 mg, 0.9 mmol) were dissolved in DMF (100 mL) under an inert nitrogen atmosphere. The mixture was stirred at 700 rpm and heated at 50 ± 5 °C for 12 h. The reactive mixture was poured into deionized water (300 mL) and the pH of the solution was adjusted to 1-2 using aqueous HCl (10% w/w), which resulted in the precipitation of a brownish solid that was vacuum filtered and purified in a chromatographic column using a mixture of dichloromethane and isopropanol (97:3 v/v) as eluent to afford Bis-HUB1 as a white solid after vacuum drying (700 mg, yield = 70%).

2.3. Gelation tests and minimum gelation concentration

Bis-HUB1 solutions (5% w/v) were prepared in the selected solvents (water, cyclohexane, dichloromethane, acetonitrile, toluene, n-hexane and ethanol) by increasing the temperature of the

initial suspension using a thermal bath, until complete homogeneity was achieved. As the resulting solutions spontaneously cooled back to 25 °C, the phase behavior of the samples was qualitatively evaluated by tube inversion. The physical state of the preparations was classified as soluble, insoluble, crystallization or gel. The tube inversion test was subsequently repeated at lower concentrations until the content of organogelator was no longer enough to prevent the solvent flow under the gravity action. These values were reported as the CGC of the resulting organogels.

2.4. Gel-to-sol transition temperatures

The gel-sol transition temperature (T_{GS}) measurements were performed on a heating plate, with temperature control. The initial temperature of the study was fixed at 24 °C. The heating rate used was 0.25 °C/min. The tested organogelator concentrations ranged from the CGC value to 5% w/v.

2.5. Hydrogen Bonding Detection Using Variable Temperature FTIR Spectroscopy (VT-FTIR)

The VT-FTIR spectra were recorded on a Bruker Vertex 70 spectrophotometer equipped with a thermostatic cell holder and a temperature-controlling unit (Specac West 6100+). One-mm thick samples of selected organogels were placed between two KBr windows to perform the experiments within a closed cell, using a spectral resolution of 2 cm^{-1} and 24 scans.

2.6. Determination of π - π Stacking Interactions Using UV-visible Spectroscopy (UV-vis)

Dilute solutions of the organogelators were prepared in some solvents where gelation occurred, as well as in a solvent where gelation was not observed. Measurements were performed on a UV-vis Cintra 303 GBC spectrophotometer, employing a 10 mm width quartz cell.

2.7. Freeze-Fracture Transmission Electron Microscopy

Transmission electron microscopy (TEM) was performed with a Philips CM12 microscope operating at 120 kV. The gel samples were placed between two copper holders and rapidly frozen in liquid nitrogen. The sample was kept frozen and transferred into a freeze-fracture apparatus (developed by Dr. J.-C. Homo) where the sample was cleaved.

2.8. Gelation test of diesel, gasoline and phase selective gelation

Gelation of diesel and gasoline was carried out following the methodology previously described in Section 2.2. The phase selective gelation test consisted in preparing a mixture of 1

mL of either gasoline (87 or 92 octane) or diesel in 1 mL of water. 50 mg of Bis-HUB1 were added to the monophasic and biphasic systems and the preparation was subjected to magnetic stirring at 600 rpm during 30 minutes at 25 °C. Gel formation was confirmed by means of the tube inversion test.

3 Results and discussion

3.1. Synthesis of the compounds

Bis-HUB1 was synthesized according to Figure 1. The bromoamide Am-HU was formed by coupling 11-bromoundecanoic acid and n-hexanamine [Figure 1(a)]. The corresponding phenol was etherified with Am-HU in phase transfer conditions with fair yields [Figure 1(b)]. The products were obtained at a scale of several grams. The complete synthesis procedure is detailed in Section 2.2.

3.1.1 Characterization of 11-bromoundecanoic acid hexylamide (Am-HU)

The final product was recovered as a yellowish solid (4.99 g, yield = 83.2%). 3.1 M. p. 58-60°C; ¹H NMR (400 MHz, CDCl₃/TMS): δ [ppm] 0.88 (t, J = 6.8 Hz, 3 H, **CH**₃), 1.28 (m, 16 H, **CH**₂), 1.41 (m, 2 H, Br(CH₂)₂**CH**₂), 1.48 (m, 2 H, NHCOCH₂**CH**₂), 1.61 (m, 2 H, CONHCH₂**CH**₂), 1.84 (quint, J = 7.2 Hz, 2 H, BrCH₂**CH**₂), 2.14 (t, J = 7.6 Hz, 2 H, NHCO**CH**₂), 3.23 (q, J = 6.8 Hz, 2 H, CONH**CH**₂), 3.40 (t, J = 6.8 Hz, 2 H, Br**CH**₂), 5.43 (s, 1 H, **NH**). ¹³C NMR (100 MHz, CDCl₃/TMS) δ [ppm]: 14.07 (CONH(CH₂)₅CH₃), 22.60 (CONH(CH₂)₄CH₂), 25.86 (CONH(CH₂)₂CH₂), 26.63 (NHCOCH₂CH₂), 28.18 (NHCO(CH₂)₂CH₂), 28.76 (NHCO(CH₂)₃CH₂), 29.31 (NHCO(CH₂)₄CH₂), 29.34 (Br(CH₂)₄CH₂), 29.39 (Br(CH₂)₃CH₂), 29.40 (Br(CH₂)₂CH₂), 29.66 (CONHCH₂CH₂), 31.52 (CONH(CH₂)₃CH₂), 32.85 (BrCH₂CH₂), 34.15 (BrCH₂), 36.96 (NHCOCH₂), 39.55 (CONHCH₂), 173.19 (NHCO). CG/MS (ret. time, s) 24.73. FTIR (ATR-diamond) ν_{max} (cm⁻¹): 3282 (νN-H), 1637 (νC=O), 1553 (ip N-H), 728 (γ(CH₂)_n, n≥4), 687 (νC-Br). MS (ESI+): m/z calcd for C₁₇H₃₄BrNO [M + H]⁺: 349.36; found: 350.19. Anal. Calcd for C₁₇H₃₄BrNO: C, 58.61; H, 9.84; N, 4.02; found: C, 59.02; H, 9.89; N, 4.27.

3.1.2 Characterization of 3,5-bis-(11-hexylcarbamoyl-undecanoxy)-benzoic acid methyl ester (Bis-HUB1)

M. p. 94°C; ^1H NMR (400 MHz, CDCl_3/TMS): δ [ppm] 0.88 (t, $J = 6.8$ Hz, 6 H, CH_3), 1.29 (m, 32 H, CH_2), 1.45 (m, 8 H, $\text{Ar-O}(\text{CH}_2)_2\text{CH}_2$, $\text{NHCOCH}_2\text{CH}_2$), 1.62 (s, 4 H, $\text{CONHCH}_2\text{CH}_2$), 1.76 (quin, $J = 7$ Hz, 4 H, $\text{Ar-OCH}_2\text{CH}_2$), 2.15 (t, $J = 1.9$ Hz, 4 H, NHCOCH_2), 3.24 (q, $J = 6.7$ Hz, 4 H, CONHCH_2), 3.89 (s, 3 H, COOCH_3), 3.96 (t, $J = 6.6$ Hz, 4 H, Ar-OCH_2), 5.42 (s, 2 H, NH), 6.63 (t, $J = 2.4$ Hz, 1 H, C3-H, C5-H, O-(Ar)CCH), 7.15 (d, $J = 2.4$ Hz, 2 H, C2-H, C6-H, $\text{COO}(\text{Ar})\text{CCH}$). ^{13}C NMR (100 MHz, CDCl_3/TMS) δ [ppm]: 14.10 ($\text{CONH}(\text{CH}_2)_5\text{CH}_3$), 22.62 ($\text{CONH}(\text{CH}_2)_4\text{CH}_2$), 25.90 ($\text{CONH}(\text{CH}_2)_2\text{CH}_2$), 26.03 ($\text{NHCOCH}_2\text{CH}_2$), 26.64 ($\text{NHCO}(\text{CH}_2)_2\text{CH}_2$), 29.20 ($\text{NHCO}(\text{CH}_2)_3\text{CH}_2$), 29.34 ($\text{NHCO}(\text{CH}_2)_4\text{CH}_2$), 29.36 ($\text{Ar-O}(\text{CH}_2)_4\text{CH}_2$), 29.39 ($\text{Ar-O}(\text{CH}_2)_3\text{CH}_2$), 29.46 ($\text{Ar-O}(\text{CH}_2)_2\text{CH}_2$), 29.54 ($\text{Ar-OCH}_2\text{CH}_2$), 29.69 ($\text{CONHCH}_2\text{CH}_2$), 31.54 ($\text{CONH}(\text{CH}_2)_3\text{CH}_2$), 37.01 (NHCOCH_2), 39.54 (CONHCH_2), 52.29 (COOCH_3), 68.30 (Ar-OCH_2), 106.54 (C3, C5, O-(Ar)CCH), 107.59 (C2, C6, $\text{OOC}(\text{Ar})\text{CCH}$), 131.79 (C1, $\text{OOC}(\text{Ar})\text{C}$), 160.14 (C4, O-(Ar)C), 167.06 (COO), 173.10 (NHCO). FTIR (ATR-diamond) ν_{max} (cm^{-1}): 3308 ($\nu\text{N-H}$), 1706 (ester $\nu\text{C=O}$), 1639 (amide I), 1537 (amide II), 1237 (as $\nu\text{C-O-C}$), 1050 (sy $\nu\text{C-O-C}$), 1182 (ester as $\nu\text{C-O}$), 1107 (ester sy $\nu\text{C-O}$), 862, 767 (oop Ar C-H), 679 (oop C-C), 718 ($\gamma(\text{CH}_2)_n$, $n \geq 4$). MS (ESI $^+$): m/z calcd for $\text{C}_{42}\text{H}_{74}\text{N}_2\text{O}_6$ [$\text{M} + \text{H}$] $^+$: 703.05; found: 703.56. Anal. Calcd for $\text{C}_{42}\text{H}_{74}\text{N}_2\text{O}_6$: C, 71.75; H, 10.61; N, 3.98; found: C, 71.68; H, 10.57; N, 4.03.

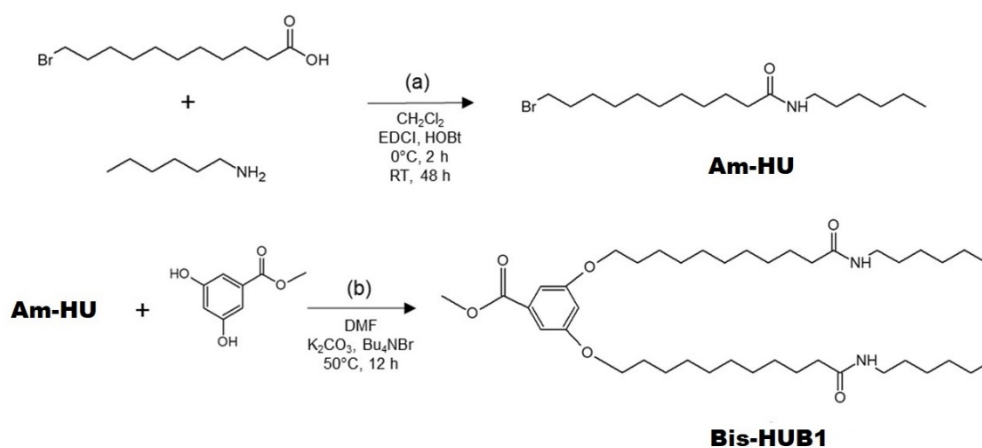


Figure 1 Synthesis scheme of (a) Am-HU and (b) Bis-HUB1.

3.2. Gelation Tests and Minimum Gelation Concentration

The gelation tests of Bis-HUB1 were performed in solvents of varying polarities at a fixed concentration of 5 % w/v. The selected solvents were acetonitrile, as an example of an aprotic polar solvent; ethanol, as a protic polar solvent; dichloromethane, as a moderately polar organic solvent; toluene, as an aromatic; cyclohexane, as a non-polar cyclic solvent, and n-hexane, as its straight-chain analogue. Additionally, the gelation tests were conducted in water. As shown in Table 1, Bis-HUB1 gels acetonitrile, n-hexane, and cyclohexane, although the gels prepared in alkanes are stable only below 0 °C.

Water was the most polar solvent used in the gelation tests according to its dielectric constant of 80.1 (Breynaert et al., 2020). The fact that supramolecular interactions that might be established between the amide groups of Bis-HUB1 would be importantly restricted by the high solvation power and dielectric constant of water (Steed et al., 2007), along with the hydrophobic nature of the alkyl chains that bear Bis-HUB1, explains the lack of hydrogelation ability of the bisamide synthesized in this study.

As reported in Table 1, gels were produced neither in dichloromethane nor in ethanol, both polar solvents that are not suitable for gel formation due to their ability to dissolve the compounds. Additionally, Bis-HUB1 did not gel toluene probably because it is able to interact with the aromatic part of the gelator and form weak H-bonds with amides (Malone et al., 1997).

Table 1 Gelation tests of Bis-HUB1 at 25 °C and CGC results—in parenthesis—, where: I = insoluble, S = soluble, G = gel, C = crystal, G* = gel at 0 °C.

Solvent	Phase behavior
Water	I
Acetonitrile	G (1.0%)
Ethanol	C
Dichloromethane	S

Toluene	S
Cyclohexane	G*
n-Hexane	G*

Interestingly, acetonitrile was gelled by Bis-HUB1. Although water and acetonitrile are both polar solvents, the dielectric constant of acetonitrile (Daniels et al., 2017) is barely half of that of water (acetonitrile= aprotic polar solvent and water=protic polar solvents); therefore, the solvophobic balance between acetonitrile and Bis-HUB1 is not as extreme as it is in water, where the compound is totally insoluble. Correspondingly, ethanol and acetonitrile are also polar solvents, but the hydroxyl group of the alcohol offers a source of hydrogen bonding that increases the solvophilic forces between the solvent and the solid particles whose amide groups may act as donor or acceptor of hydrogen bonding; on the contrary, the polarity of acetonitrile is not conferred by hydrogen bonding sites and, consequently, as it was observed in the gelation tests, solvation does not occur in acetonitrile as it does in ethanol. The organogelator Bis-HUB1 was incapable of forming gels in the presence of dichloromethane (aprotic polar solvent) and toluene (non-polar solvent), but at the same time, it presented a good gelation capacity in cyclohexane and hexane (non-polar solvents, at 0 °C). The gelation of acetonitrile, cyclohexane, and hexane could be attributed to the fact that these solvents are not as prone to interact with Bis-HUB1 molecules as the rest of the tested organic solvents do. Since gelator-gelator intermolecular interactions were favoured instead of solvent-gelator interactions, gelation prevailed over solvation in those solvents (Babu et al., 2014).

In order to assess the viability of these newly synthesized materials, their gelation test and minimum gelation concentration results were compared with the results presented by some longer and more complex compounds in recent years. (Delbecq et al., 2020) synthesized six new amidoamines bearing long hydrocarbon chains, -OH groups and amines, and used them in gelation tests at 4% w/v and room temperature, finding the formation of gels in various solvents including n-hexane and cyclohexane. (Lin et al., 2016) analysed the gelation capacity of the low molecular weight gelator 1,3:2,5:4,6-tris(3,4-dichlorobenzylidene)-D-mannitol (G1) at concentration of 2% (w/v); this compound has aromatic rings and chiral cores and it showed no gelation capacity in

common solvents such as water, cyclohexane, acetonitrile, etc. (Yousofi et al. 2019) studied the gelation capacity of a new supramolecular and microporous organic gelator, 1-(6-isocyanato)-3-octadecylureahexyl-N-formyl supported on melamine-terphthalaldehyd microporous organic framework (1,4-DMB@4Mel@8(ODUHNF)), in its structure presents many urea functional groups, aromatic rings and hydrocarbon chains. It had the capacity to gelate toluene at concentrations of 0.010 g/mL (1% w/v). (Jiao et al., 2013) analysed the gelation performances of the imide compound known as CH-PY (bolaform cholesteryl imide derivative with aromatic spacer) at concentration of 1.5-2% and they found the following results: acetonitrile-insoluble, toluene-partially gel and n-hexane-partially soluble. This compound has a voluminous structure containing chiral cores and azobenzenes. (Bachl et al., 2015) synthesized 3 tetrapeptides bearing side-chain azobenzenes: A4, bis-A4, and F-A4 and they reported the following minimum Gelation Concentration, MGC (% w/v) results: toluene- A4: 2.0 ± 0.2 , Bis-A4: 0.5 ± 0.1 and F-A4: 4.4 ± 0.3 , their structures contain more amide groups and more azobenzene groups in comparison with Am-HU and Bis-HUB1. (Tsai et al. 2013) analysed the gel forming abilities of biscalixarenes, which contain several aromatic rings, hydrocarbon chains and amide groups. The biscalixarenes gelled alcoholic solvents with CGC ranging from 0.05 to 0.13 (w/v %). In this study, all the gelators were predissolved in other organic solvents and treated with hexanes or long chain alkanes. Comparing the results obtained by other researchers with those presented in Table 1, it was observed that Bis-HUB1 is capable of forming gels of cyclohexane and hexane at 5 % (w/v) and even of acetonitrile at 1% (w/v). This material is a promising organogelator with the advantages of lower molecular weight, simpler chemical structure (Figure 1) and a low minimum gelation concentration (1-5% w/v). Its insolubility in water makes it suitable for a further study in oil spill remediation, see Section 3.7.

3.3. *Gel-to-sol transition temperatures*

The relation between Bis-HUB1 concentration in acetonitrile and its T_{GS} is displayed in Figure 2. The shape of the diagram shows that even if T_{GS} levels off as the concentration of Bis-HUB1 increases, it still depends on the gelator concentration, since there is no miscibility gap nor phase separation between the solvent and the gelator (Christ et al., 2016); contrarily, it presents what has been called a pseudo-plateau by some authors (Berret et al., 1994). This kind of phase diagram

can be derived from a Van-Laar type equation. The gel-sol transition enthalpy (ΔH_{gel}) was estimated from the van't Hoff equation (Suzuki et al., 2016), presented in equation 1, where c is the organogelator concentration in the organogel, T_{GS} is the gel-sol transition temperature, R is the universal gas constant and ΔS° is the standard variation of entropy.

$$\ln c = -\frac{\Delta H_{gel}}{R} \left(\frac{1}{T_{GS}} \right) + \frac{\Delta S^\circ}{R} \quad \text{Equation (1)}$$

By linearly representing $\ln c$ versus $1/T_{GS}$, the calculated ΔH_{gel} for the Bis-HUB1 gel in acetonitrile was 63 kJ/mol. According to literature, the obtained enthalpy corresponds to the amount of energy expected for a supramolecular system interacting through hydrogen bonds as well as other non-covalent forces like π - π stacking and Van der Waals interactions (Griffiths et al., 2010; Schmidt et al., 2002), given that the energy for a typical amide-amide hydrogen bond usually does not exceed 21 kJ/mol (Schmidt et al., 2002). According to (Suzuki et al. 2016), who synthesized 5 simple organogelators with organic salt structures by mixing of L-amino acid dodecyl esters and azobenzene-4-carboxylic acid, the T_{gel} was directly related to the gelator concentration. The T_{gel} depends on the gel-sol transition enthalpy (ΔH_{gel}), their values are dependent of the strength of the interaction between gelator molecules and/or fibers, since the more intense the non-covalent forces, the more energy demanded by the system to experience a phase transition. The transition temperature (T_{gel}) and the gel-sol transition enthalpy (ΔH_{gel}) of acetonitrile/gelators values were: gelators 1-2= 55 °C, 93 and 95 kJ/mol; gelators 3-4= 50 °C, 52 and 50 kJ/mol; and gelator 5= 45 °C, 53 kJ/mol. The gelators with higher thermal stability has stronger interactions.

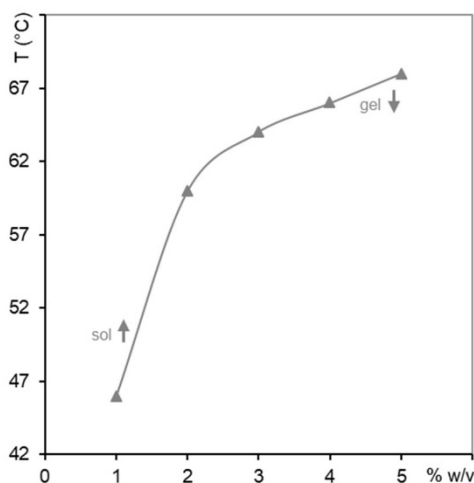


Figure 2 Gel-sol transition temperature as a function of gelator concentration of Bis-HUB1 in acetonitrile.

3.4. Hydrogen Bonding Detection Using Variable Temperature FTIR Spectroscopy (VT-FTIR)

The VT-FTIR spectra of the gel of Bis-HUB1 in acetonitrile, at 25 and 61 °C is shown in Figure 3. The N-H stretching band is located between 3300 cm^{-1} and 3330 cm^{-1} , in the associated band zone. It corresponds to H-bonds between amide groups. In these spectra, no free N-H bonds are visible. The amide also shows only one amide I mode shifting from 1637 to 1641 cm^{-1} . The ester groups have a low frequency, around 1707 cm^{-1} , which cannot be explained only by the conjugation with the benzene but may be by an interaction between esters (Palui et al., 2008). Actually, upon melting the ester experience a shift toward higher frequencies, which proves that the ester is involved in the formation of the gel. As a conclusion all the amide groups in Bis-HUB1 are H-bonded, which confer stability to the Bis-HUB1-acetonitrile gels and explains its high T_{Gs} values compared with similar oligoamide organogels reported in literature (Schmidt et al., 2003).

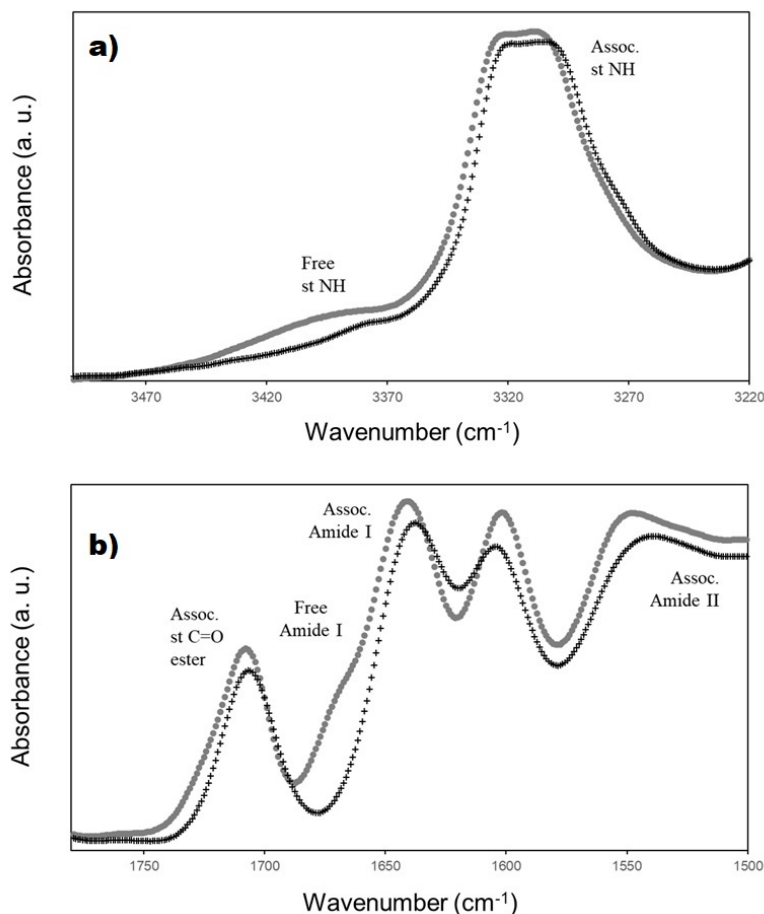


Figure 3 VT-FTIR spectra of gels of Bis-HUB1 in acetonitrile at 2% in (a) vN–H region, and (b) vC=O region. (+) at 25 °C and (•) at 61 °C.

3.5. Determination of π - π stacking interactions using UV-visible spectroscopy (UV-vis)

The UV-vis spectra of diluted solutions of Bis-HUB1 in n-hexane, cyclohexane, and acetonitrile, where gelation took place, as well as in ethanol, where gelation was not observed, are shown in Figure 4.

The spectra of Bis-HUB1 solutions exhibit two major absorption bands due to the different substituents on the benzene (Korshin et al., 1997). As seen in Figure 4 and Table 2, the solution of Bis-HUB1 in ethanol had two λ_{\max} located at 252 nm and 306 nm. In acetonitrile the spectrum is the same, with the same maxima. The spectra in cyclohexane and n-hexane have a different shape, with a more pronounced shouldering peaks and shifts of 2 nm and 5 nm, respectively. Although stable gels at room temperature were not obtained in n-hexane or cyclohexane when Bis-HUB1 was used as gelling agent, these results suggest that π - π stacking between the aromatic rings of the

bisamide molecules in fact occurred, but they were not strong enough to induce the supramolecular growth of a gel-like structure, possibly due to the steric hindrance entailed by the second amide substituent in the aromatic ring.

Comparable magnitudes of spectroscopic shifts have been reported in reference studies (Basak et al., 2015; Ran et al., 2015), where the formation of J- or H-aggregates in their systems was concluded depending on the direction of the shifts; however further studies should be conducted in the gel state in order to prove the formation of such aggregates in the studied Bis-HUB1-acetonitrile organogel.

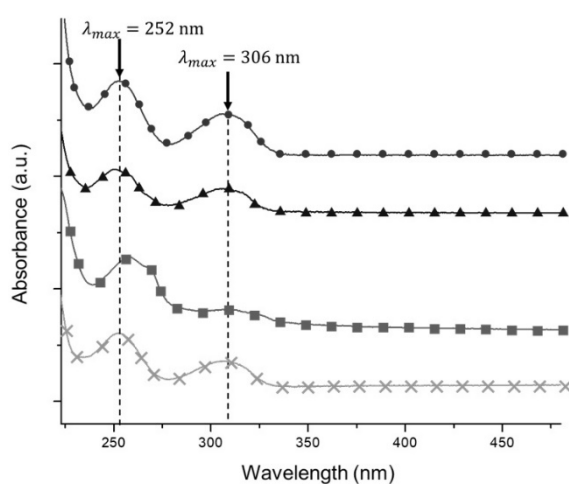


Figure 4 UV-vis absorption spectra at 25 °C of Bis-HUB1 diluted solutions in (●) ethanol, (▲) cyclohexane, (■) n-hexane and (×) acetonitrile.

3.6. Freeze-Fracture Transmission Electron Microscopy (FF-TEM)

The structure of the self-assemblies formed in the organogels of Bis-HUB1 in acetonitrile at 3%, was examined by FF-TEM and is presented in Figure 5.

Figure 5 does not suggest the formation of fibrillary arrays in the Bis-HUB1-acetonitrile organogel, but rectangular platelets of approximately 100 nm width were detected. The formation of these structures suggests that the network of Bis-HUB1 molecules in the acetonitrile organogel consists of well-organized arrays of crystalline nature. For example, (Nazemi, et al., 2017) described rectangular platelets of comparable size and shape formed by the self-assembly of crystallizable blends of block copolymers.

Even if the bisamide has two amide groups, this feature does not affect significantly the ability of the molecules to establish supramolecular interactions conducting to the formation of well-defined fibers at the microscale. As demonstrated in reference works, variations in the length of the amide radicals of the molecule do not affect the morphologic features of the self-assembled structures in bisamide gelators similar to Bis-HUB1 (Schmidt et al., 2003), but when the amide radicals were kept constant, as the length of the alkyl chain of the ester increased, the morphology of the aggregates changed from flat to helical and twisted ribbons (Simon et al., 2013).

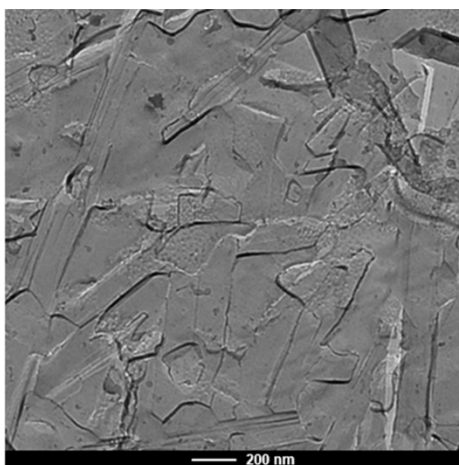


Figure 5 Transmission electron micrographs of freeze-fractured organogels of Bis-HUB1 in acetonitrile at 3%.

Similar structures were found by (Laupheimer et al. 2015), who synthesized a binary system n-decane/12- hydroxyoctadecanoic acid (12-HOA). It was found that some samples had more fiber-like than those expected for a lower gelator mass fraction (1.5 wt %). The study showed that the concentration of the gelator is not directly related to the density of fibres, this situation could occur due to the cooling of the sol to the gelling temperature (25 °C). Also, the obtained morphology could be attributed to the assembly mode and forces between Bis-HUB1 and acetonitrile, also by the hydrogen bonding or π - π stacking between the aromatic rings of the bisamide molecules, see Section 3.5 (Jiao et al. 2013; Schmidt et al. 2003).

3.7. Gelation test of diesel, gasoline and phase selective gelation

As shown in Figure 6(a) Bis-HUB1 was capable of forming gels of gasolines GM (87 octane), GP (92 octane), and diesel as well in mixtures of water/solvent 1:1 with 50 mg or 0.05 g / 2 mL of mixture (2.5 % w/v) of Bis-HUB1. Although the Bis-HUB1 gelation test of alkanes was just

successful at 0 °C, the more complex mixture of hydrocarbons that comprises the gasoline composition appears to be important for making the gasoline gelation possible, without the necessity of cooling the preparations below 25 °C. For instance, the formation of H-bonds between Bis-HUB1 molecules in acetonitrile gels has been demonstrated in this study (Section 3.2); correspondingly, the polar fraction of compounds existing in the tested fuels may favor the H-bond formation and conduct the gelation process.

Moreover, Bis-HUB1 proved to be an efficient selective gelator of GP gasoline from a water/gasoline mixture as a result of a mechanical agitation stimulus, as seen in Figure 6(b). This is important not only because it shows that Bis-HUB1 is a smart gelator possessing the ability of responding to external stimuli different from thermal processing, but also because it proves that even though Bis-HUB1 is not as structurally complex as other reported selective gelators (Bachl et al., 2015; Ran et al., 2017), it is also potentially useful for recovering gasoline from spills in aqueous media.

Similarly, (Yousofi et al. 2019) studied the gelation of crude oil products: gas (0.004 g/mL or 0.04 % w/v) and diesel (0.002 g/mL or 0.02 % w/v) of organic gelator, 1-(6-isocyanato)-3-octadecylureahexyl-N-formyl supported on melamine-terphthaldehyd microporous organic framework (1,4-DMB@4Mel@8(ODUHNf)) at room temperature. Additionally, (Bachl et al. 2015) analysed the gelation of crude oil products: A4: Gas 2.4 ± 0.2 g/mL and diesel 2.0 ± 0.2 ; Bis-A4: Gas 2.5 ± 0.2 g/mL and diesel 2.0 ± 0.2 ; and F-A4: Gas 4.5 ± 0.5 g/mL and diesel 2.4 ± 0.2 at room temperature. Comparing these results with those obtained during the experimentation, the Bis-HUB1 molecule demonstrated that it is a competitive material for further researches in oil spill remediation. In our investigation, competitive results of fuel gelation were observed compared to the research of (Tsai et al. 2013), which reported the preparation of biscalixarene 1 (10.0 mM) in ethyl acetate and its gelation capacity with gasoline fuels was analysed. It gelled almost all available gasoline fuels: diesel, pump oil, and silicone oil, except petrol. Its CGC ranged from 0.097 to 0.37 (w/v %). They studied the gelation of biscalixarene 1 (10 mM in ethyl acetate) at room temperature and a 1:1 (v/v) mixture seawater/hexane (or various oils) and it was found that the mixture was equilibrated for a few minutes, and then, the oil was gelled/separated from seawater.

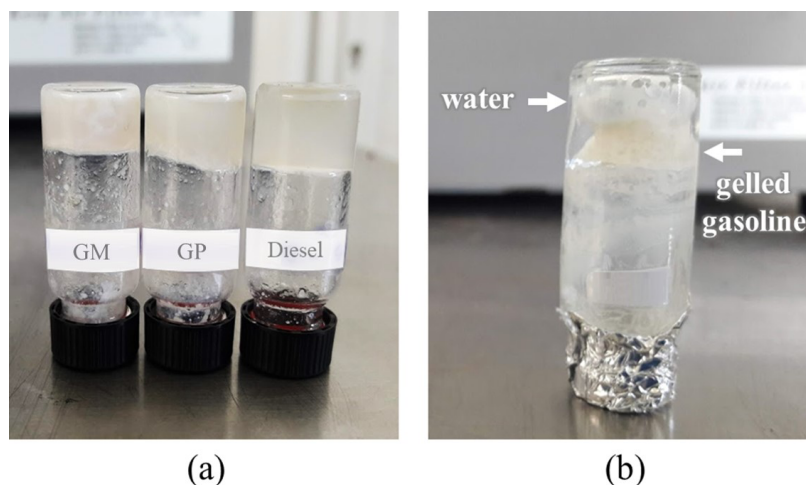


Figure 6 (a) Gelation tests of Bis-HUB1 in GM (87 octane gasoline), GP (92 octane gasoline) and diesel, from left to right, at 5% and 25 °C, and (b) Phase-selective gelation of GP gasoline from water/gasoline mixture at 25 °C triggered by mechanical agitation.

4 Conclusions

A low molecular mass bisamide organogelator was synthesized and characterized at large scale and high purity levels. Additionally, the product was studied for water cleaning applications, particularly, for gelation and collecting hydrocarbons from spills. Although organogels of n-hexane, cyclohexane and acetonitrile were obtained, just the acetonitrile organogel was stable at room temperature. The enthalpy values estimated using the van't Hoff equation predicted the formation of intermolecular hydrogen bonds in the Bis-HUB1 organogel; this assumption was further confirmed by a VT-FTIR study that allowed to conclude that almost all of the amide groups of Bis-HUB1 were hydrogen bonded and it also evidenced the presence of dipole-dipole interactions between esters, which explains the high transition temperatures of Bis-HUB1 gels in acetonitrile. A UV-vis spectroscopy analysis demonstrated that weak π - π stacking interactions were established between Bis-HUB1 in alkanes.

The structural study revealed that Bis-HUB1 formed rectangular platelets in the acetonitrile gel. Finally, the bisamide gelator was useful for gelling gasoline and diesel, and furthermore, it exhibited selectivity to gel the gasoline phase from a water/gasoline mixture, which opens its potential application as solidifier for oil recovery from spills. The further research of this material

is encouraged due to their significant gelation capacity, in order to solve the water pollution problem.

Declarations

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Code availability (software application or custom code): Not applicable.

Ethics approval (include appropriate approvals or waivers): Not applicable.

Consent to participate (include appropriate statements): Not applicable.

Consent for publication (include appropriate statements): Not applicable.

Authors' contributions: Samuel Zapién-Castillo, Nancy P. Díaz-Zavala, Philippe J. Mésini, and Jessica I. Lozano-Navarro conceived and designed the experiments, also analyzed the data, wrote the paper and revised the written translation of article; Samuel Zapién-Castillo and Jorge J. Montes Patiño performed the experiments; Josué F. Pérez-Sánchez and José A. Melo-Banda analyzed the data. All authors have read and agreed to the published version of the manuscript.

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