

Supramolecular self-assembly studies and spectroscopic analysis of oligomers used for the removal of pollutants from wastewaters

Estudios de autoensamblaje supramolecular y análisis espectroscópico de oligómeros empleados para la remoción de contaminantes en aguas residuales

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Abstract

The oil spills in the oceans have caused severe damage, many of these are irreversible generating the loss of marine ecosystems, such is the case of the British Petroleum company in 2010. Therefore, there is a need to produce materials that contain or prevent the spread of the hydrocarbon in the ocean, in addition to being able to recover the crude oil quickly and effectively. Various materials have been designed focused on environmental remediation, specifically in the treatment of contaminated water. In this work, organogelling materials were synthesized from alkoxides such as Methyl 4-hydroxybenzoate, Propyl 4-hydroxybenzoate, Ethyl 4-hydroxybenzoate and the alkyl halides 1-bromohexadecane and 1-bromotetradecane, all of them analyzed by FTIR spectroscopy. In addition, gelation tests were performed in protic, aprotic and fatty acid solvents. Organogels, have a solid appearance at the nanoscale and extends into a liquid phase. Consequently, if there is a close contact between the solvent and the nanogel structure, a highly effective surface is obtained, providing a kind of solid phase in contact with highly polluting liquids. The importance of this work lies in the feasibility of using oligomers as removers or sequestrants of unwanted contaminants in effluents.

Oligomers, Contaminants, Remediation

Resumen

Los derrames de petróleo en los océanos han ocasionado severos daños, muchos de estos son irreversibles generando la pérdida de ecosistemas marinos, tal es el caso de la empresa British Petroleum en el año 2010. Por ello, existe la necesidad de producir materiales que contengan o impidan el esparcimiento del hidrocarburo en el océano, además de poder recuperar el crudo de manera rápida y efectiva. Se han diseñado diversos materiales enfocados a la remediación ambiental, específicamente en el tratamiento de aguas contaminadas. En este trabajo, se sintetizaron materiales organogelantes a partir de alcóxidos como el Metil 4-hidroxibenzoato, Propil4-hidroxibenzoato, Etil 4-hidroxibenzoato y los haluros de alquilo 1-bromohexadecano y 1-bromotetradecano, todos ellos analizados mediante espectroscopía FTIR. Además, se realizaron pruebas de gelificación en solventes próticos, apróticos y ácidos grasos. Los organogeles, tienen una apariencia sólida a nanoescala y se extiende en una fase líquida. En consecuencia, si existe un contacto cercano entre el solvente y la estructura del nanogel, se tiene una superficie altamente efectiva, proporcionando una especie de fase sólida en contacto con líquidos altamente contaminantes. La importancia de este trabajo radica en la factibilidad de emplear los oligómeros como removedores o secuestrantes de contaminantes no deseados en efluentes.

Oligómeros, Contaminantes, Remediación

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1. Introduction

Water is one of the most precious natural resources in the world and in spite of being so abundant in our planet, only 3% is contemplated for human consumption while 97% is distributed in seas and oceans. As a consequence of this problem and considering the unforeseen environmental accidents of this nature, there is a need to create materials to contain crude oil spills in the sea and thus recover it quickly and efficiently. The contamination problem in southern Tamaulipas and northern Veracruz affects both northern Veracruz (Pueblo Viejo) and the municipalities of Tampico, Cd. Madero and Altamira in Tamaulipas. The effects of the contamination have been on health, where in 1995 there were 700 cases of cholera, and on fish production, especially in the lagoon of Pueblo Viejo^[1].

Geomorphological aspects are determinant in the system's problems. Sediments originating in the Sierra Madre Oriental reach this zone, which tend to be deposited over geological time in low-gradient zones. On the other hand, the existing low gradient allows seawater to enter the estuary at high tide conditions, which generates an interaction between suspended solids, of fluvial origin, and dissolved solids, of marine origin^[1].

Likewise, the coastal waters of the Gulf of Mexico show increasing levels of contamination derived from the discharge of industrial waters from the Altamira area, mainly^[1].

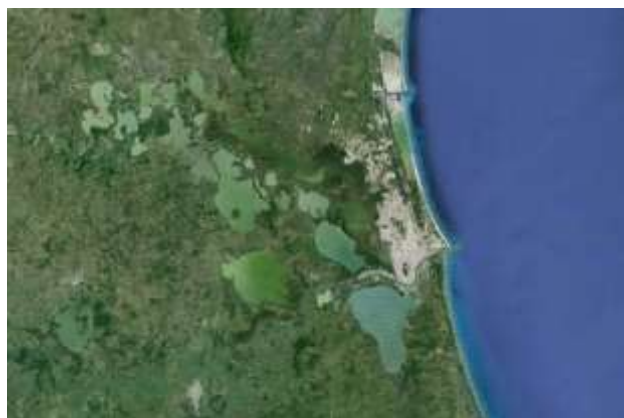


Figure 1 Aerial view of the Tamesí River Lagoon System, the city of Tampico, and the Gulf of Mexico
 Source Google Earth, Ponce and Aguilar 2019^[1].

The importance of this work lies in obtaining environmentally friendly materials, which allow the fast, efficient and accurate removal of pollutants in water bodies or effluents and thus reduce the level of contamination of the same, coming from carboxylic acids and amides which are susceptible to form bonds by physical forces, specifically hydrogen bonds, specifically hydrogen bridges, as well as pi-pi attractions and Van der Waals^[II] forces from the hydrocarbon chains that allow access to the oil constituents in a selective way that are possible to create selective systems of non-polar organic liquids and oils that are capable of achieving a gelation of a specific mixture containing two phases. Some researchers have succeeded in obtaining low weight molecules capable of gelling in oil spills, dyes, heavy metals and chemical weapons anions Figure 2.

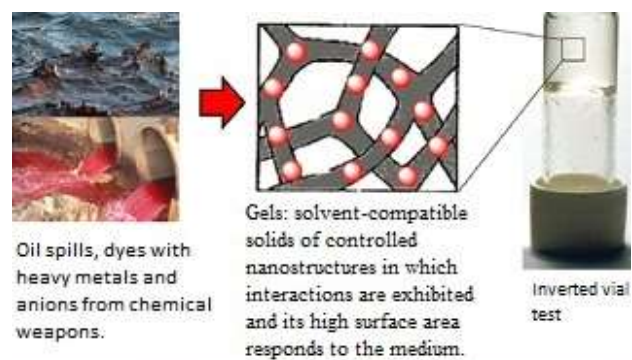


Figure 2 Self-assembled gel-phase materials for environmental remediation
 Source Okesola and Smith 2016^[111]

Organogelators exhibit thermotropic properties and this generates potential interest in their application as sensors, templates for nanostructure fabrication, biochemistry, rheology modifiers. Although many types of oligomers have been developed, there is little reference to the ability of gelators to selectively self-assemble in one solvent into another solvent in a given mixture. This is interesting when one of the solvents in the mixture is water. Oligomers possess self-assembly properties and form fibrillar objects in different organic solvents.

A gelling agent is a substance that when added in very small proportions, less than 1%, to a liquid transforms it into a gel. When the liquid used is an organic solvent, the gel is called organogel.

Simple organic molecules self-organize into supramolecular polymers of a fibrillar nature, whose structure is maintained by non-covalent interactions. Oligomers derived from metal alkoxides, as well as alkyl halides, retain the fibrillar structure without collapsing upon solvent removal, a property only attributed to oligomers containing chiral carbons in the structure. In this work, oligomers without chiral carbons were designed, the materials were analyzed by FTIR characterization technique to identify functional groups and due to this condition, self-assembly and thermo-reversibility tests allowed obtaining the latent heats of each molecule.

Organogels can be distinguished from hydrogels by their predominantly organic solvent. The gelation process involves the self-assembly of low molecular weight organogels (LMOG) to give a fibrillar polymer-like appearance, which immobilize the organic solvent forming a three-dimensional network of cross-links or entangled chains for chemical and physical gels^[IV].

Fibers are stabilized by weak interactions such as hydrogen bridges, Van der Waals forces. Many factors such as steric effects, rigidity and polarity can counteract self-assembly. Control over the gelation process and the conception of new gelling molecules remain important challenges in the search for new organogelators^[VI,VI].

2. Methodology for the synthesis of molecules

2.1 Synthesis of C1C16, C2C14, C3C16 molecule

– Method of preparation of the oligoether:

The reagents were used as received: methyl 4-hydroxybenzoate (Aldrich), N,N-dimethylformamide (DMF), potassium carbonate K₂CO₃, alkyl bromide (1-bromohexadecane, 1-BHD) and nitrogen as inerte gas (Figure 3). The oligomer was synthesized by Williamson's method from a phenolic derivative (alkoxybenzoates) and an alkyl halide.



Figure 3 Reaction equipment using an inert médium
Own source

A solution was prepared with the corresponding alkoxide in dimethylformamide (DMF) to which potassium carbonate was added. After having reacted for 2 hours at a temperature between 60-65°C, the corresponding bromide (1-bromohexadecane) was added and allowed to react for a further 8 hours at the same temperature. At the end of the reaction, the contents of the flask were allowed to cool to room temperature or immediately poured into a beaker containing very cold water with ice (Figure 4).



Figure 4 Obtaining the C1C16 oligomer
Own Source

The product is recovered with the formation of a white material, which crystallizes immediately and is filtered (Figure 5). The filtrate is left to dry on a crystallizer for 3 to 4 days in a desiccator to eliminate any percentage of moisture (Figure 6).



Figure 5 Washing and crystallization of the oligomer derived from Alkoxybenzoates and alkyl halides
Own Source



Figure 6 Washing and crystallization of oligomer derived from alkoxybenzoates and alkyl halides
Own source

3. Characterization by FTIR infrared spectroscopy C1C16, C2C14, C3C16 and gelation tests.

3.1 FTIR Characterization

This spectroscopy is based on the absorption of IR radiation by vibrating molecules. Two basic categories of vibrations can be distinguished: tensile and bending vibrations. Tension vibrations are changes in the interatomic distance along the bond axis between two atoms. Bending vibrations are caused by changes in the angle formed by two bonds. The samples were characterized in a Fourier transform spectroscopy (FTIR) apparatus. The effect of the hydrocarbon chain of the ester group in the organogel will be examined using FTIR spectroscopy. The analyzed molecules presented functional groups such as the double bonds of the aromatic ring, -COOR, -CH₃, -CH₂. The synthesized oligomers were evaluated in a Fourier Transform Infrared Spectrophotometer Perkin Elmer Spectrum 100 model with the ATR technique with diamond reflection unit and a resolution of 4 cm⁻¹ and 16 scans.

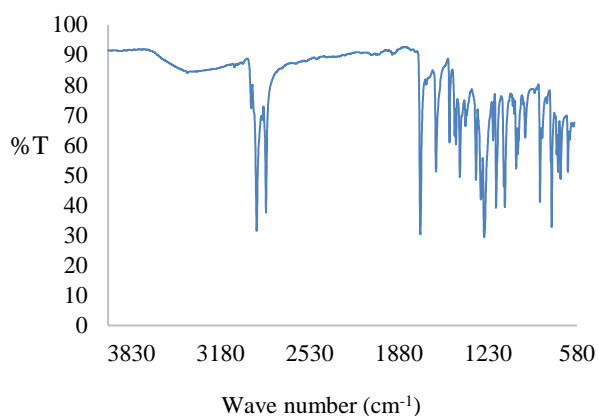
3.2. Gelation tests

Gelation tests were performed in duplicate on C1C16, C2C14, C3C16 molecules in different solvents, starting from an initial concentration of 5%. The molecules were dissolved in diethylether DMF, methanol, ethanol, heptane, propylene carbonate, ethyl acetate, isopropanol, hexane, olive oil, castor oil and propylene glycol. The gelation tests were performed by heating the oligomer at the indicated concentration until a homogeneous solution was formed, leaving a transparent solution inside the vial and allowing it to cool for a few seconds (in some samples for minutes) at room temperature, observing different behaviors: gel, precipitates and homogeneous solutions. When the gel state was obtained, the inverted vial method was used and its formation was verified.

4. Results

4.1 Infrared Results

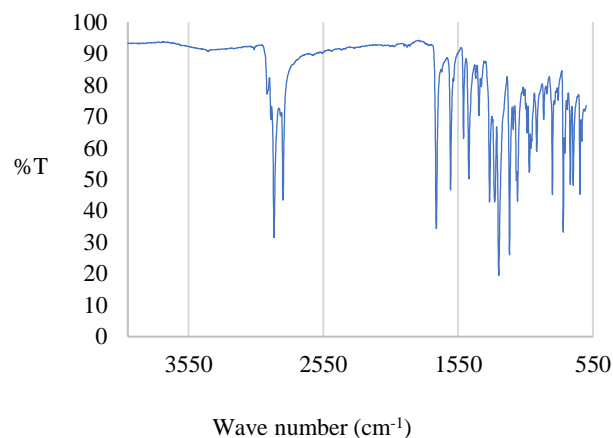
The characteristic groups of the synthesized molecules C1C16, C2C14 and C3C16 are observed in graph 1; two middle bands are presented which correspond to the elongations of the C-H bonds, these appear in the range of 3020-2850 cm^{-1} attributed to the $-\text{CH}_3$ and $-\text{CH}_2$ groups whose bending at 1497-1350 cm^{-1} , provide the certainty of the existence of these groups; at 762 cm^{-1} it was possible to determine the effect of the long alkyl chains; the ester group at 1725 cm^{-1} , the aromatic ring at 1609 cm^{-1} has an average C=C bond elongation band corresponding to the vinyl ether group, the ether group is located in the range of 1310-1000 cm^{-1} ; a strong split band of asymmetric elongation of the C-O-C group in the vinyl ethers appears in the range of 1275-1230 cm^{-1} and is corroborated by the appearance of the symmetric elongation signal at 1075- 1020 cm^{-1} .



Graph 1 Fourier Transform infrared spectrum of C1C16 molecule
Own Source

The following spectrum (graph 2), containing information about the function groups shows the infrared spectra of the C3C16 molecules, it is observed that the band size increases as the chain length increases in the oligoether, the characteristic band of the methyl and methylene groups at 2973-2833 cm^{-1} , at 1712 cm^{-1} the ester group and the double bond of the aromatic ring 1604 cm^{-1} at 1511 and 1475 cm^{-1} a shift of the bends is observed for methyls and methylenes, this is attributed to the increase in the size of the alkyl chain for the ester group. The band attributed to the ether groups is observed in the 1150-1085 cm^{-1} range which is generated by the asymmetric stretches. This band is usually observed near 1125 cm^{-1} .

Finally, the ether group band occurs at 1280 and 1264 cm^{-1} . It is noticeable in all three spectra that as the alkyl chain increases the spectral band shifts increasing from 1255 to 1259 cm^{-1} .



Graph 2 Fourier Transform infrared spectrum of C3C16 molecule
Own Source

4.3 Results of the gelation tests

The synthesized materials were subjected to gelation tests in different solvents initially at a single concentration equal to 5%, each test in duplicate, with the purpose of verifying the solvents in which the C1C16, C2C14, C3C16 molecules presented gelation and self-assembly processes.

The importance of this test lies in the fact that it is possible that by designing organogels from non-chiral carbons, it will be possible to create molecules that present resistance to collapse at the moment of making the templates, or by being used as sequestering agents of environmental pollutants, it will be possible to easily remove them from the toxic or harmful structures that are contained in the effluents or polluted bodies of water.

Once the gelation result was obtained, the samples were prepared again in these solvents varying the concentrations from 1 to 10%, in 1 ml vials mixed with each solvent (0.6 ml). The organogel was left to stand at room temperature for 20 minutes and was gently heated until a homogeneous solution was obtained, then it was slowly cooled and kept at 10°C (Figure 7). The gelation capacity was evaluated using the vial inversion methodology and stored for 24 hours at 20°C; the vial was inverted for 1 hour and if the material did not flow, it was considered gelled (Tables 1 to 3).



Figure 7 Gelation of the C3C16 molecule
Own Source

C1C16 (5%)		
	Vial 1	Vial 2
Diethylether	I do not gel	I do not gel
DMF	I do not gel	I do not gel
Cyclohexane	I do not gel	I do not gel
Methanol	If I gel	If I gel
Ethanol	I do not gel	I do not gel
Heptane	I do not gel	I do not gel
Propylene carbonate	I do not gel	I do not gel
Ethyl acetate	I do not gel	I do not gel
Isopropanol	I do not gel	I do not gel
Hexane	I do not gel	I do not gel
Olive oil	I do not gel	I do not gel
Castor oil	I do not gel	I do not gel
Propylene glycol	I do not gel	I do not gel

Table 1 Results of gelation tests at 5% of C1C16
Own Source

C2C14 (5%)		
	Vial 1	Vial 2
Diethylether	I do not gel	I do not gel
DMF	I do not gel	I do not gel
Cyclohexane	I do not gel	I do not gel
Methanol	If I gel	If I gel
Ethanol	I do not gel	I do not gel
Heptane	I do not gel	I do not gel
Propylene carbonate	If I gel	If I gel
Ethyl acetate	I do not gel	I do not gel
Isopropanol	I do not gel	I do not gel
Hexane	I do not gel	I do not gel
Olive oil	I do not gel	I do not gel
Castor oil	I do not gel	I do not gel
Propylene glycol	I do not gel	I do not gel

Table 2 Results of gelation tests at 5% C2C14
Own source

C3C16 (5%)		
	Vial 1	Vial 2
Diethylether	I do not gel	I do not gel
DMF	Si gelifico	Si gelifico
Cyclohexane	I do not gel	I do not gel
Methanol	If I gel	If I gel
Ethanol	If I gel	If I gel
Heptane	I do not gel	I do not gel
Propylene carbonate	I do not gel	I do not gel
Ethyl acetate	I do not gel	I do not gel
Isopropanol	I do not gel	I do not gel
Hexane	I do not gel	I do not gel
Olive oil	I do not gel	I do not gel
Castor oil	I do not gel	I do not gel
Propylene glycol	I do not gel	I do not gel

Table 3 Results of gelation tests at 5% of C3C16
Own Source

With the results obtained, it was possible to determine that the oligomers that presented gelation. The organogelation was carried out in different organic solvents showing reversibility of the materials and exhibiting that the self-assembly is carried out by supramolecular forces, since when performing such tests and forming the organogels they presented the phase change when an increase in temperature was applied, returning to the colloidal state as it cooled down.

It was observed that the solvents of similar chain to the oligomer did not gel and were soluble as toluene, cyclohexane, hexane and pentane; on the other hand, the solvents used of short polar chains, such as methanol, ethanol, isopropanol, acetonitrile, propylene carbonate and diethylenetriamine presented gelation.

5. Funding

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6. Conclusions

The self-assembled materials gave rise to the formation of fibers of different lengths when varying the primarily polar solvent, this is shown in the images whose morphology varies from short fibers as in alcohols to ribbons, in solvents whose polar factor increased. In the molecules studied in this work, the forces driving self-assembly can be originated through π - π , dipole-dipole and Van der Waals interactions. The length of the alkyl chains causes solvent compatibility and gelation efficiency. As future work, it is intended to collect effluent liquids from the conurbation area to measure the efficiency of these materials in the removal of environmental pollutants.

As future work, it is necessary to perform gelation tests on gasoline, petroleum oil, kerosene, phenols and other common compounds found in water bodies and effluents in order to carry out the application of the materials.

These water bodies and effluents will be georeferenced in order to determine the water and effluent sampling sites in the metropolitan area and to be able to apply the supramolecular oligomers with the proper treatment of the samples.

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