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Remediation of Marine Oil Spills and Water Pollution using Low Molecular Weight Organo-Gelators

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Abstract

Low molecular weight organo-gelators (LMOGs) can be employed for efficient removal of oil, toxic dyes, metal ions as well as organic pollutants from water bodies. An effective self-assembly assisted by non-covalent interactions holds the key to formation of a three-dimensional network capable of immobilizing the oil phase. The authors here present a personal perspective on the basic understanding and credibility of such gelation systems.

Keywords: Organo-gelators; Oil spills; Water pollution; Biocompatibility; Futuristic aspects; Organo gel

Abbreviations: LMOGs: Low Molecular Weight Organo-Gelators, PSOG: Phase Selective Organo-Gelation

Introduction

Molecular gels are self-assembled systems where the solute molecules (gelators) interact and combine via various non-covalent interactions such as H-bonding, van der Waals forces, π-π bonds, hydrophobic interactions, charge transfer, etc. and form one dimensional fibers, which on aggregation, form 3D assemblies which can trap a solvent, forming a gel. Gels are visco-elastic materials [1-3] which display flow characteristic on application of strain. And as the saying goes, if you wish to identify if a given substance is a gel or not, well, "If it looks like Jell-O, it's a gel…" [4] Gels can defy gravity and an inverted vial containing a gel will likely resist its ability to flow. The underlying principle seems very simple, yet it gets complex as we dig in deeper. Since it depends on a variety of factors whether a particular molecule will congeal a particular solvent or not, most of the gelators have been discovered by serendipity and not by design. The mechanism at molecular level is not even fully understood till today. As was rightly quoted by D. J. Lloyd, "the colloid condition, the gel, is easier to recognize than to define" [5].

Gels are broadly classified based on solvents gelled by them; hydrogels, where the solvent being gelled is water and organo gels, where organic solvents are involved. The gelator molecules can belong to various classes like polymers, multi-component systems, small molecules, peptides and many more! They are employed for various high-tech applications in molecular sensing, energy storage, catalysis, tissue engineering, drug delivery, templating, cosmetics, dyes, adhesives, thickening agents, and many more [6]. They also have a great potential to be used as smart materials as they are highly versatile systems which can respond to light, heat, ultrasound waves, pH, etc. They inevitably stand out because of their indispensability, biocompatibility, and programmability.

LMOGs for Tackling Oil Spills

Marine oil spills are the result of natural or accidental discharge of crude oil and petrochemicals in the water bodies. In April 2010, the Deepwater Horizon oil rig suffered an explosion in the Gulf of Mexico and leaked millions of barrels of crude oil in the ocean. This, however, was not the first report of marine oil spill. According to statistics, more than a thousand oil spills are reported every year. While they are not necessarily as dreadful as the Deepwater Horizon, they still cause long-term damage and pose serious threat to marine ecosystem. The consequences can be disastrous, which contribute to environmental pollution, severely affected marine flora and fauna, spillage of non-renewable fossil fuels, to name a few. As far as tackling of oil spills is concerned, there are various methods available like absorption, dispersion, burning, bioremediation (use of microbes that feed upon and digest the oil), fertilizers, etc. [7-10] Among these, the efficiency of supramolecular gelation is unsurpassed, as it involves gelation of all the oil present on the water surface, which can be skimmed off in a semi-solid gel form and heated to retrieve back the oil.

The thermoreversibility and non-destructive nature of these systems offer added advantage as they facilitate recovery of oil, and at the same time, the gelator can be recycled and reused.

[11-15]. Although the idea of employing LMOGs for treating oil spills has been known since the 1970s, it was only in 2001 when a solid report of amino acid based LMOG by Bhattacharya et. al. burst the bubble around the theory. Gels were reported in aliphatic hydrocarbons as well as commercial oils even in biphasic oil-water mixtures [16]. Since then, a variety of different molecules such as organic salts (multi-component systems) [17-21] amides [22,23] esters [24] polymers [25,26] urea-based moieties [27], amino acid derivatives (peptides) [28-31] cholesterol-based moieties [32,33] sugar-based moieties [34-37] etc. have been exploited for their ability to selectively gel organic solvents in presence of water (figure 1).

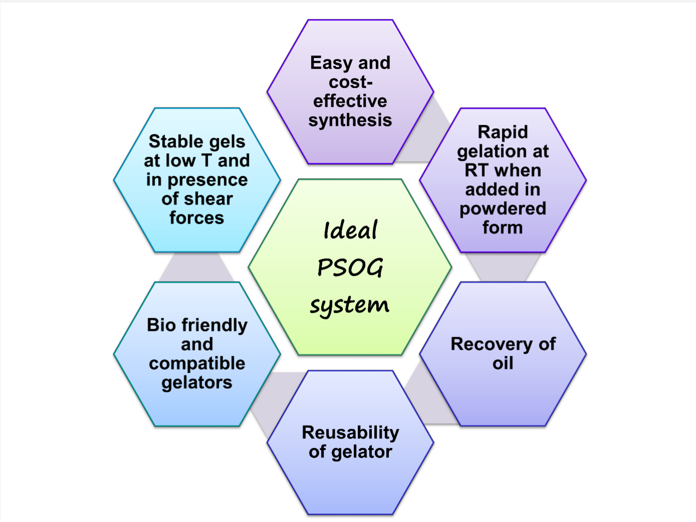

Figure1: Desirable properties in an ideal PSOG system.

Even though, there are certain practical problems that make the use of LMOGs for phase selective organo-gelation (PSOG) ambiguous. For e.g., such systems involve a heat-cool cycle or use of a co-solvent which is ideally miscible in both phases. This allows an even dispersion of gelator molecules in dissolved form, which can be advantageous in forming a stronger gel. However, use of co-solvent causes contamination of both, organic as well the aqueous phase, and thus, can end up doing more harm than good. Hence it is ideal for a gelator to selectively congeal oil in presence of aqueous media at room temperature, preferably in powdered form. Another key point is, most of the studies reporting PSOG focus on gelation of kerosene, petrol, diesel, engine oil, etc. Crude oil-based reports are limited in literature because it remains unavailable to most of the researchers. The reason behind raising this point is, crude oils can contain natural acids and other elements which can impede gelation behavior [21], and since such systems are highly sensitive towards the constituents of both phases, we can comfortably say that systems congealing petrol, diesel and kerosene may not necessarily form gels in crude oil.

As far as designing of PSOGs is concerned, there are various reports in literature which highlight different aspects of molecules, in terms of interactions, crystal engineering, structure-property relationship, etc. [38-43]. Nonetheless, the key to a successful design should inevitably consider all these facets. The amphiphilicity of gelator in any biphasic system governs its ability to interact with both the phases. It also regulates the formation of fibers which self-assemble via various interactions to immobilize a solvent. It is believed that hydrophobic interactions control the self-assembly in hydrogels and hydrophilic interactions control the gelation behavior in organic solvents. In presence of a biphasic system, such interactions can be disabled, and a highly amphiphilic gelator is likely to remain at the interface, interacting with both the phases, and consequently, it will fail to gel either solvent or invariably form an emulsion [44-47].

LMOGs for Controlling Water Pollution

Supramolecular gels can be very efficiently employed for sequestration of dyes dissolved in aqueous medium. The self-

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assembled fibers of an organo gel can interact with the dye molecules present in water. This causes the dyes molecules to be absorbed by the gel, thereby eliminating them from water. In certain reports, gelation has been carried out along with the dye molecules. This can significantly decrease the concentration of pollutant dye from water, with impressive adsorption efficiencies. The same concept can be applied for efficient and selective uptake of heavy metal ions, anions, nano particles, and even certain organic pollutant species [11,48]. Many of the reported studies have also developed mechanisms of 'switch-on/off' gelation, where gelation is triggered or obstructed in presence of the active moieties. This can ease recovery of precious ions and contribute to tackling water pollution at large.

Conclusions and Futuristic Aspects

In summary, much progress has been made in PSOG and its extended high-tech applications. However, there are many aspects which can be developed to enhance our understanding of topics in hand and this article touches only the tip of iceberg. An ideal designing paradigm is highly favorable for getting much needed insights into the practical applications for crude oil gelation, interactions between the pollutant ions/species and gelator fibers, reusability of gelators, selectivity of gelation and pollutant uptake, etc. The design of new LMOGs is always challenging due to multiple factors such as 1 tides, 2. continuous flow of hot/cold air may bring disruption to the formation of organo gel containing fuel/crude oil 3. especially in the hostile marine environment. The design of an ideal candidate which can exhibit gelation behavior calls for a universal gelling compound in all petrochemicals, such as crude oil and commercial fuels with a high mechanical strength and sol-gel transition induced by sunrays. Moreover, a stable gel containing fuel can assist in transportation as well. These factors can contribute to the ultimate challenge of creating designer, self-programmable soft materials with desired applications.

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