First report of phase selective gelation of oil from oil/water mixtures. Possible implications toward containing oil spills

**Santanu Bhattacharya*† and Yamuna Krishnan-Ghosh**

*Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India.
E-mail: sb@orgchem.iisc.ernet.in*

From a two-phase mixture of water and oil (either commercial fuel or pure organic solvent), a simple amino acid derivative, *N*-lauroyl-L-alanine has been shown to be able to gelate the oil phase selectively; SEM and FT-IR provided molecular level insights into the process of gelation.

Much has been achieved in the field of polymeric gels and their applications.[1] Although several excellent non-polymeric *low molecular mass* organogelators have been developed,[2,3] the ability of an organogelator to gelate one solvent in preference to another from a given mixture has still not been evidenced. This becomes an even more daunting task when one of the solvents in such a mixture is water. This is because, in contrast to their macromolecular counterparts, the network structure formed by low molecular weight organogelators are often held together by non-covalent interactions such as hydrogen bonding.[3] Understandably, water competes for the hydrogen bonding sites in the gelator molecule, thereby disrupting the self-association of the gelator and ruining gelation. We discovered that a fatty acid
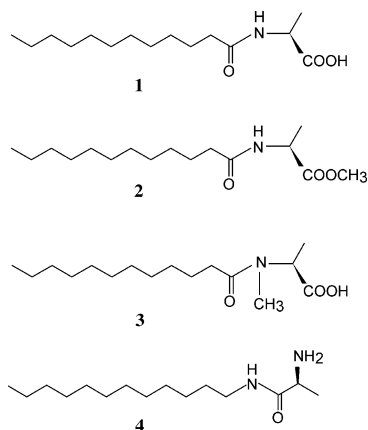
derived amino acid, *N*-lauroyl-L-alanine, **1**, is a simple and effective system for the selective gelation of non-polar organic solvents such as aromatic and aliphatic hydrocarbons. Herein we report for the first time an organogelator, which is capable of achieving solvent-specific gelation from a two-phase mixture. To derive a proper structure–property correlation, related compounds **2–4** were also synthesized.‡

First the efficiency of **1** in gelating various aromatic and aliphatic hydrocarbon solvents was examined§ (Table 1). For a series of *n*-alkanes with $6 < n < 12$, the MGC passed through a maximum for $n = 8$, and another minimum was reached for $n = 16$, where *n* is the number of C-atoms in the aliphatic hydrocarbon. The gels formed in aliphatic hydrocarbons were translucent in nature while those formed in aromatic solvents were found to be transparent. Since the above solvents also form

major constituents of petrol, we found that **1** could indeed gelate a wide range of commercial fuels (Table 1).

Representative SEM¶ of the gels of **1** obtained from either *n*-heptane (Fig. 1A) or toluene (Fig. 1B) shows the presence of a network of fibers of varying thicknesses. In the heptane gels, a profusion of thin fibers (0.5–1.5 µm) was seen while in toluene gels individual fibers of regular thickness (3.0 µm) appeared to merge into thicker fibers (6–15 µm). Solvent molecules get entrapped in the fibrous networks due to surface tension resulting in gelation.

We then investigated selective gelation of a discrete volume of such fuels by **1** when it is present in a two-phase system. A mixture of double-distilled water (2 mL) and an oil (2 mL) was taken in a test tube and **1** (10 mg) was added to the two-phase mixture. Compound **1** was solubilized either by heating or by injection of an ethanolic solution of **1** leaving the mixture to equilibrate. Remarkably, as soon as rt was attained, the oily layer was found to be completely gelated leaving the aqueous layer unaffected. Even upon standing for ~ 1 week, both the phases remained intact with their respective states of gelation and non-gelation. When the experiment was repeated with periodic or continuous violent agitation (a model 'oil-spill situation') the above mixture formed an emulsion which, upon cooling to rt, rapidly solidified into a mass where the phase

Table 1 Gelation properties of **1** (1 mmol) and minimum gelator concentration (MGC) in g L^{-1} (gelator/organic solvent) necessary for gelation of various organic solvents at 25 °C

Organic liquid	MGC	Organic liquid	MGC
n-Hexane	7.0	Benzene	8.0
n-Heptane	2.6	Toluene	3.5
n-Octane	2.4	*o*-Xylene	5.1
n-Decane	2.5	*m*-Xylene	5.5
n-Dodecane	2.7	*p*-Xylene	2.7
n-Hexadecane	2.4	Mesitylene	2.2
Isooctane	3.4	Cyclohexane	4.0
Petrol	11.9	CCl$_4$	8.8
Kerosene	3.2	1,2-Dichlorobenzene	5.0
Paraffin oil	5.1	Carbon disulfide	5.9
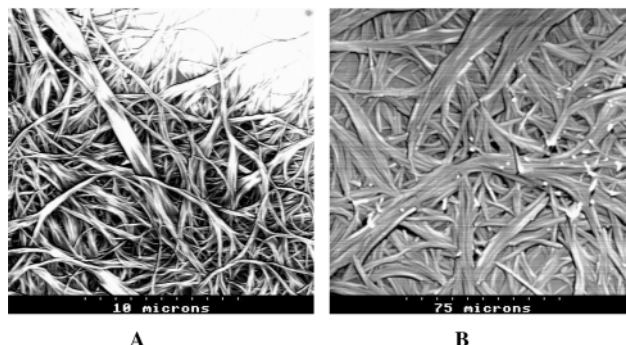
Fig. 1 SEM of gels of (A) *n*-heptane and (B) toluene with **1**.

boundaries were indistinct. Heating of this gelled emulsion to > 50 °C resulted in the 'melting' of the mass which separated into discrete aqueous and organic layers. When this was allowed to cool undisturbed, as before only the organic layer was gelated selectively. Similarly, a given volume of commercially available petrol could be gelated from a two-phase mixture. Importantly the gelation was unaffected even in the presence of (a) NaCl (at various concentrations) or (b) chelation inducing metal salts (*e.g.* CuSO$_4$), or (c) oxidizing agents (*e.g.* KMnO$_4$) or (d) other impurities present in water from natural sources (not shown).

Next, the roles of various functional groups involved in the self-assembly process were investigated by blocking one by one the hydrogen bonding sites in **1** *via* chemical modification. First the carboxylic acid (-CO$_2$H) in **1** was converted to its methyl ester, **2**. Then the amide moiety (-NH-C(O)) in **1** was subjected to *N*-methylation to give **3**. Interestingly, neither **2** nor **3** induced any gelation. Thus the presence of both the -CO$_2$H and the secondary amide (-NH-C(=O)) appear to be essential for self-association of the monomer into fibers (Fig. 1) a necessary prerequisite for gelation.

In order to understand the precise roles of the -CO$_2$H and -NH-C(=O) residues in **1** in the process of gelation, detailed FT-IR studies were carried out.‖ First, FT-IR spectra of (a) the solid (KBr pellet) from a dried benzene gel of **1**, (b) solutions of **1** (*c* = 60 mg mL^{-1}) in benzene and (c) in a non-gelatable solvent such as CHCl$_3$ were compared (not shown). The amide and the –CO$_2$H moieties in **1** are as strongly hydrogen bonded in the gel state as they are in the solid state. Benzene does not interfere with the intermolecular association. The *amide I* band in the gel state was almost as strongly hydrogen bonded as in the solid (1646 cm^{-1}). However, in CHCl$_3$ the *amide I* band (1669 cm^{-1}) evidenced a weakly hydrogen bonded species probably between the oxygen of the amide carbonyl and the acidic H of CHCl$_3$. This is confirmed by efficient gelation of CCl$_4$ by **1**. Thus solvents capable of hydrogen bonding *suppress* gelation in these systems by disallowing the self-assembly process.

The -CO$_2$H sites of **1** in both solvents form dimers of comparable strength (1732 cm^{-1}). Thus the factor controlling gelation of **1** seems to be hydrogen bonding at the amide sites (-N–H···(O)=C–N–H···(O)=C-), which is significantly affected by the polarity and protic nature of the solvent. However, the strength of the *amide I* band is considerably weaker in CHCl$_3$ (1669 cm^{-1}) than in benzene (1648 cm^{-1}). It is this difference in strength that most probably determines whether the solvent promotes or inhibits perpetuation of the superstructure. In addition to the amide site, the availability of the free -CO$_2$H is mandatory for the dimer formation leading to gelation. This was confirmed with **4** where the free amine cannot form analogous dimers and despite the presence of amides, the gelation did not occur.

In summary, in order to exhibit gelation, the molecule must have the capacity to self-assemble in three-dimensions to form fibrous networks. Self-assembly of **1** is evident from SEM. IR studies show that this process involves at least two interactions (-CO$_2$H and (O)=C–N–H) where each residue promotes the formation of a supramolecular array. In water, due to the presence of a lipophilic alkyl chain, **1** exerts a hydrophobic effect[4] and excludes water. Additional stabilization of such aggregates most likely originates from Van der Waals contacts of the polymethylene chains. This promotes the self-organization of **1** and in the process it is able to gelate hydrocarbon-based fuels or solvents even in the presence of water. While the present system is interesting, the necessity to heat and cool the samples in order to achieve phase separation significantly limits its use for the containment of oil-spills. Clearly issues such as requirement of heating to achieve gelation have to be addressed before a real-life application is possible. Nevertheless the present system demonstrates its unique ability to confer phase-selective gelation of toxic solvents from complex mixtures.

Notes and references

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