# New lyotropic phases (thermally-reversible organogels) of simple tertiary amines and related tertiary and quaternary ammonium halide salts

**Liangde Lu and Richard G. Weiss***

*Department of Chemistry, Georgetown University, Washington, DC 20057, USA*

**Small concentrations of some structurally simple tertiary amines and related tertiary and quaternary ammonium halide salts form viscoelastic, thermally reversible gels with a wide variety of organic liquids.**

The vast body of research on surfactant aggregation, including that from the common phosphoglycerides containing an ammonium group, has focused primarily on phases involving water and other polar or protic media. Even in mixed solvent systems, the aqueous/polar component determines in large part the way the surfactant molecules assemble since they are good hydrogen bond donors/acceptors. We report here that some structurally simple amine and ammonium surfactants aggregate into novel assemblies in the absence of water or other polar liquids (*i.e.* under conditions where hydrogen bonding is *not* present).

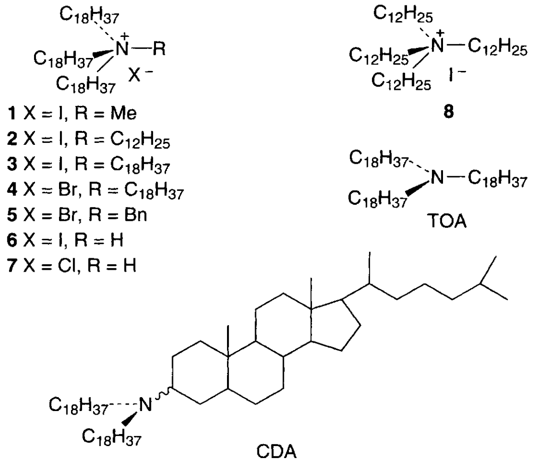
When tertiary amines, such as trioctadecylamine (**TOA**) or the α- or β-anomer of cholestanyldioctadecylamine (**CDA**), or related tertiary and quaternary ammonium halide salts (Scheme 1)† are dissolved by heating in an organic liquid and then cooled, we find that viscoelastic, thermally-reversible gels can form in which the amines aggregate in long, thin, interlocking crystalline strands[1–3] (Fig. 1). The liquid component remains isotropic, but is immobilized by surface tension.[1] Although there is precedence for gelation of organic liquids by ionic species[4,5] and amides,[6,7] this behaviour appears to be unprecedented for *simple*, low molecular weight amines and ammonium salts[8–10] even when they are dimeric or trimeric.[11–13] It indicates that factors different from those governing the aggregation of salts[14,15] in aqueous media are operative.

To test gelation, an amine and liquid are heated in a sealed glass tube until the solid dissolves and then are cooled. The macroscopic manifestation of successul gelation is the absence of observable flow when a sample is inverted. In many cases, gels were hazy or bluish due to the Tyndall effect. Gel stability is based upon the gelation temperature ($T_g$; measured by the 'inverted flow' method)[16] and the length of the period necessary to observe macroscopic phase separation when samples are incubated in sealed vials at room temperature.

At 2.5 mass%, the β-anomer of **CDA** forms a precipitate with dodecane and gels with Dow-Corning 704 silicone oil (tetramethyltetraphenyltrisiloxane) or pentan-1-ol, while the α-anomer produced only solutions. However, a translucent gel was obtained from 5 wt% α-**CDA** and silicone oil. The structurally simpler gelator, **TOA**, yields very stable gels with silicone oil or pentan-1-ol, very unstable gels with benzene and no gels with alkanes. In that regard, the periods of stability of gels of **3** in undried and azeotropically-dried benzene are not very different. Also, thermal gravimetric analysis of **2** between 40 and 90 °C showed a loss of <0.013% sample weight, corresponding to less than one molecule of water per molecule of **2**. Traces of water do not appear to be important to this gelation,[5,17] and, more generally, hydrogen-bonding to the lone-pair of electrons of the tertiary amines is not necessary for gelation.

Attempts to gel a variety of liquids with **1** are collected in Table 1. Gels of benzene or toluene are stable for only *ca.* 30 min with **6**, for hours with **1**, for weeks with **3** and for months with **2**. By contrast, **3** does not gel dodecane, but **1**, **2** and **6** do very efficiently. Both **1** and **2** make very stable gels with silicone oil, but **3** and **6** lead to precipitates. Pentan-1-ol forms the most stable gels with **6** followed (in order of decreasing stability) by **2**, **3** and **1**. These results illustrate the marked influence that the gelator structure and the nature of the liquid have on the network of gelator strands[1–3,18–20] and the stability of the gels.

Pairwise comparisons of **3** and **4** or **6** and **7** provide a probe of the influence of counterions on gelator properties. Unlike the iodide **3**, the bromide **4** (and **5**) gels dodecane and silicone oil; its gels with toluene, benzene and pentan-1-ol are much more stable than those employing **3**. However, whereas **6** gels dodecane and pentan-1-ol, the chloride **7** produces only macroscopically phase-separated mixtures with these liquids.



**Scheme 1**

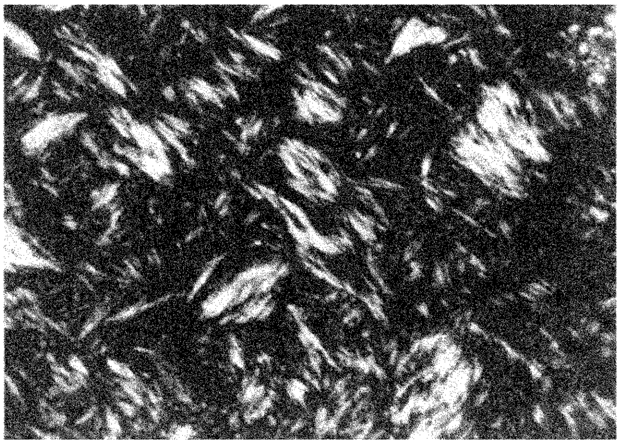


**Fig. 1** Optical micrograph (×500) between crossed polars of the gel phase of 6.0 mass% of **2** in dodecane at room temperature

Of the two 'spherical' quaternary ammonium iodides, **8** is the superior gelator with almost all of the liquids examined, including dodecane and silicone oil (not gelled by **3**) and benzene and toluene (gelled less well by **3**). However, at 3.4 mass% (the concentration of **3** that led to a turbid gel), **8** remained dissolved in pentan-1-ol.

It follows from the nature of the gel phases[1–3] that a necessary (but insufficient) requirement is that the neat gelator molecules be solids at the temperatures of their gels. Thus, the smallest tri(alkyl)amine capable of making gels of the type described here at or above room temperature must have longer chains than tridodecylamine, mp 15.7 °C.[21] However, there is no apparent correlation between $T_c$, the clearing temperatures of the neat ammonium salts (and tertiary amines) of Scheme 1 and the $T_g$ of their gels. Pertinent data for the ammonium salts that gel dodecane are included in Fig. 2. At 3–4 mass% of gelator, the $T_g$ values seem to be in the plateau region[1] and amenable to comparisons. The salt **1** has the highest $T_c$, but its $T_g$ values are lower than those of **4** and **8**. The tetraoctadecylammonium salt with the higher $T_c$, **3**, has much lower $T_g$ values. We have observed that many gelators are polymorphous,[1–3,18] and that the molecular packing in crystals from solvent recrystallization can be different from that in the strand networks of gels.[20] Also, gelation temperature is very dependent upon gelator solubility in the liquid component; the relationship between the $T_g$ values of two gelators has been inverted by placing them in liquids of different polarity.[22] Thus, no correlation between $T_c$ and $T_g$ should be expected in many cases. We also find that some of the molecules in Scheme 1 are mesomorphic.‡ Again, there is no correlation between gelator efficiency and the ability of gelators to exist in more than one non-isotropic condensed phase.

**Table 1** Gels of methyltrioctadecylammonium iodide **1**

| Liquid | Mass% of gelator | Phase | Stable period at room temp. |
|---|---|---|---|
| Cyclohexane | 3.7 | Precipitate[a] | |
| Dodecane | 3.0 | turbid gel[b] | 3 months |
| Hexadecane | 2.1 | turbid gel [a] | 3 months |
| Toluene | 4.0 | translucent gel[a] | 2 h |
| Benzene | 4.0 | translucent gel[a] | 2 h |
| Dow-Corning 704 silicone oil | 2.5 | transparent gel[c] | > 2 months |
| Propan-1-ol | 4.3 | precipitate[a] | |
| | | turbid gel[b] | 1 h |
| Pentan-1-ol | 5.0 | precipitate[a] | |
| | | turbid gel[b] | 4 h |
| Acetonitrile | 3.3 | precipitate[a] | |
| Dimethyl sulfoxide | 2.5 | transparent gel[a] | 20 min |

[a] Cooled from isotropic solution to room temperature (room temp.) in air. [b] Cooled from isotropic solution in an ice bath. [c] Cooled from isotropic solution to room temp. after a co-solvent, $CH_2Cl_2$, was evaporated; the solid could not be dissolved when heated directly in silicone oil.

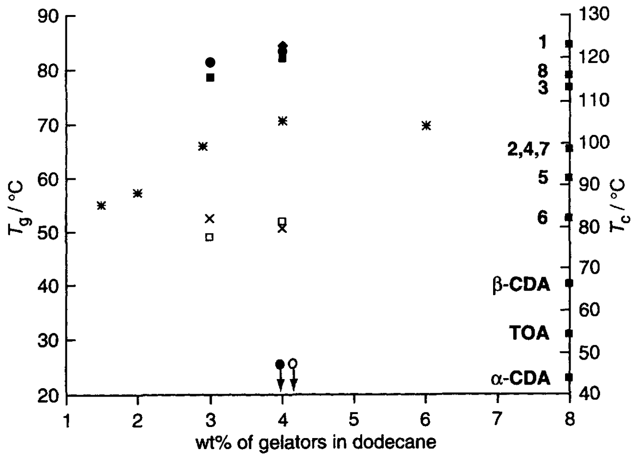


**Fig. 2** Neat gelator clearing temperatures ($T_c$) and median gelation temperatures ($T_g$) *vs.* gelator concentration in dodecane: **1** (×), **2**(*), **3**(●), **4**(■), **5**(○), **6**(□) and **8**(⧫). The arrows indicate gels formed at subambient temperatures.

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## Footnotes

† TOA was synthesized from octadecylamine by two cycles of amide formation with octadecanoyl chloride and reduction with lithium aluminum hydride. The syntheses of the α- and β-anomers of CDA have been described elsewhere.[4] Except for the commercially available **4** and **8**, the salts were prepared by standard $S_N2$ reactions of **TOA** and an excess of alkyl halide. Their structures were confirmed by infrared and NMR spectral analyses.

‡ Compounds **2** and **5** are the only thermotropic liquid–crystalline quaternary ammonium halides with more than two long alkyl chains of which we are aware. They are *amphitropic* as well by virtue of their ability to exhibit both thermotropic and lyotropic order.[12]

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