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Self-assembled organogels formed by monoalkyl derivatives of oxamide

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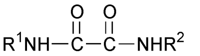
The monoalkyloxamide amphiphiles self-assemble to form ordered bilayer aggregates in a number of organic liquids and gelatinize the liquids.

In recent years the study on the gelation of organic solvents by low molecular weight organic compounds has been growing into a challenging research field.[1–4] Some attempts have been made to correlate the properties of the gels and the structures of the gelators.[5–7] Nevertheless, to date, only a limited number of small molecular gelators have been found and it is impossible to select a molecule that will definitively gel a selected liquid.[1–7] It has been known that some amphiphiles containing amide groups and chiral centers can gel a number of organic liquids even at a very low concentration, while those lacking chiral centers or racemic compounds usually exhibit no gelling ability.[2] Herein, we report simple diamide amphiphiles, monoalkyloxamide containing no chiral centers, which can form ordered bilayer aggregates in a number of organic liquids and gelatinize the liquids.

The oxamide derivatives, **1**–**7**,† used here were prepared in our laboratory. A typical procedure for studying gel formation ability is as follows: a weighed sample was mixed with an organic liquid (1 mL) in a sealed test tube and the mixture was heated until the solid dissolved. The resulting solution was cooled at 25 °C for 2 h and then the gelation was studied. Upon formation the organogel is stable and the tube can be inverted without any change of shape of the organogel.



$$R^1NH-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-NHR^2$$

1 $R^1 = C_{14}H_{29}$, $R^2 = H$ **5** $R^1 = C_{14}H_{29}$, $R^2 = C_4H_9$
2 $R^1 = C_{18}H_{37}$, $R^2 = H$ **6** $R^1 = R^2 = C_{12}H_{25}$
3 $R^1 = C_{12}H_{25}$, $R^2 = H$ **7** $R^1 = R^2 = C_4H_9$
4 $R^1 = C_4H_9$, $R^2 = H$

The minimum gel concentrations of **1** necessary for gelation are summarized in Table 1. From Table 1, it is clear that **1** can form stable physical organogels and gelatinize a number of organic fluids even at a very low concentration. For example, the amounts of **1** necessary to gel one litre of carbon tetrachloride, benzene, toluene, *o*-xylene and dichloromethane are 3, 3, 3, 4 and 6 g, respectively.

The FT-IR spectrum of the KBr pellet of **1** is similar to that of the toluene gel, suggesting that the pattern of hydrogen bonding in the gel is close to that in the crystal. The FT-IR spectrum of the toluene gel of **1** is characterized by bands near 3386 (ν_{asNH2}), 3214 (ν_{sNH2}) and 1692 cm^{-1} ($\nu_{\mathrm{C=O}}$ of primary amide) which are close to those of solid oxamide.[8,9] It has been known that the oxamide crystal has triclinic layer structure and the molecules within the layers are linked together by hydrogen bonds.[10] Therefore, it suggests that in the gel the primary amide groups (-CONH$_2$) of the amphiphiles are connected with each other by hydrogen bonds in the same way as in solid oxamide. FT-IR measurement also reveals a shift of NH stretching and secondary amide I ($\nu_{\mathrm{C=O}}$) bands from 3440, 1680 cm^{-1} for a free secondary amide group (-NHCO-) to 3315, 1648 cm^{-1}, respectively.[11] These changes demonstrate that hydrogen bonds have formed between neighboring secondary amides. The above FT-IR results indicate that in the gel three self-complement intermolecular hydrogen bonds have been formed between an oxamido-group and its neighboring ones, and thus they form a hydrogen bond network.

The TEM image of a toluene gel of **1** is shown in Fig. 1. It reveals a number of fibers, juxtaposed and intertwined by several long slender aggregations with widths of *ca.* 30–100 nm. The X-ray diffraction patterns (Fig. 2) of the gel cast film show periodical diffraction peaks, indicating that **1** indeed assembles into an ordered structure. The long spacing (D) of the aggregate obtained by the XRD method is about 3.27 nm, which is smaller than twice the evaluated molecular length of **1** (2.35 nm, by the CPK model) but larger than the length of one molecule of **1**. According to the XRD and FT-IR results, it can be deduced that the gel aggregates consist of a repeating bilayer unit, which bears the head-to-head packing model and highly tilted alkyl chains relative to the bilayer

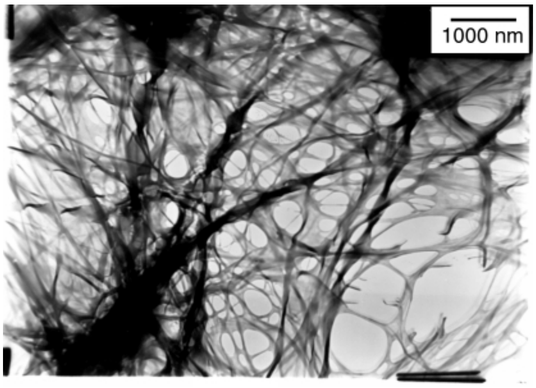


Fig. 1 TEM image of a toluene gel of **1** (4 g L^{-1}). The sample was prepared by picking up the gel on a carbon grid.

Table 1 Minimum gel concentration, *c*, of **1** (g L^{-1} solvent) necessary for gelation at 25 °C

Solvent	*c*	Stable period[a]	Solvent	*c*	Stable period[a]
Carbon tetrachloride	3	> 3 Months	Benzene	3	> 3 Months
Toluene	3	> 3 Months	*o*-Xylene	4	> 3 Months
Dichloromethane	6	> 3 Months	Acetonitrile	5	> 3 Months
1,2-Dichloroethane	6	> 3 Months	Aniline	6	> 3 Months
Tetrachloroethylene	6	> 3 Months	1,1,2-Trichloroethane	6	> 3 Months
Epichlorohydrin	5	> 3 Months	1,1,2,2-Tetrachloroethane	6	> 3 Months

[a] Stable period: the time which a gel persists in a sealed tube at 25 °C.

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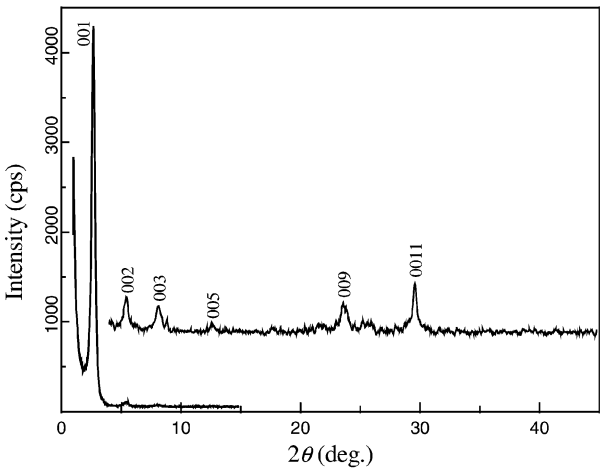

Fig. 2 XRD pattern of a cast film from toluene gel of **1**. (The XRD pattern has been adjusted by subtracting the diffraction of glass substrate in the range of (2*θ*) 16–32°).

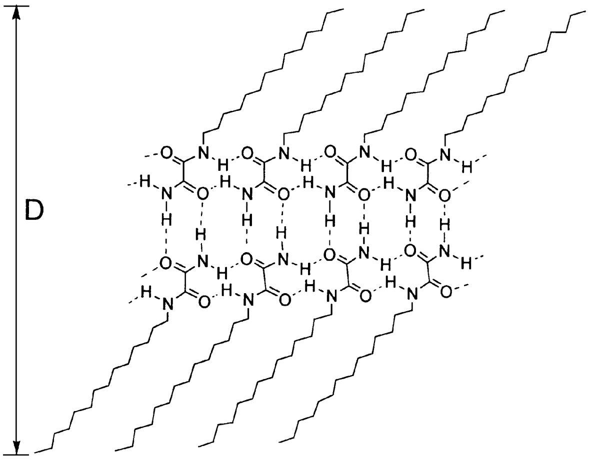

Fig. 3 Local microstructure of the bilayer aggregates of **1** in organogel.

normal (Fig. 3). Within the bilayer unit, the amphiphiles are connected with intra- and inter-layer hydrogen bonds.

The gelling abilities of some structurally related compounds, **2**, **3** (gel-forming) and **4**–**7** (non-gel-forming), have been inspected. None of the related compounds involving *N*,*N*′-disubstituted oxamide exhibit gelling ability. It may be due to the fact that after substituting one of the two hydrogen atoms of the primary amide by an alkyl group, no interlayer hydrogen bonds between the head-to-head arrangements can be formed and the amphiphiles fail to self-assemble to form ordered bilayer aggregates. Therefore the intermolecular hydrogen bonding is unable to meet the need for gelation. Furthermore, the introduction of a long lypophilic chain is essential for gelation, since organogels fail to form when the tail chain is shortened to four carbon atoms. From these observations and analyses, it can be concluded that: (i) gelling ability strongly depends on the oxamido-group; (ii) the hydrophile–lypophile balance is a significant factor for gelation; (iii) the formation of the ordered bilayer aggregates plays an important role in gel-forming.

In conclusion, this paper has shown that simple diamide amphiphiles, monoalkyloxamide, can form ordered bilayer aggregates, through intermolecular hydrogen bonding in a number of organic liquids, which are juxtaposed and interlocked by van der Waals interaction, and finally gelatinize the organic liquids.

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Notes and references

† Alkylamine reacts with diethyl oxalate in a molar ratio of 1:8 in EtOH at 70 °C for 4 h to give *N*-alkyloxamethane‡. The compounds, **1**–**7,** were prepared by reacting *N*-alkyloxamethane with excess concentrated ammonia (for **1**–**4**) or corresponding alkylamine (for **5**–**7**) in EtOH at 30 °C for 3 h. Satisfactory ^{1}H NMR data were obtained for all oxamide derivatives after recrystallization.

‡ The IUPAC name for oxamethane is oxamic acid, ethyl ester.

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