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Understanding the Role of H-Bonding in Self-Aggregation in Organic Liquids by Fatty Acid Amphiphiles with a Hydrocarbon Tail Containing Different H-Bonding Linker Groups

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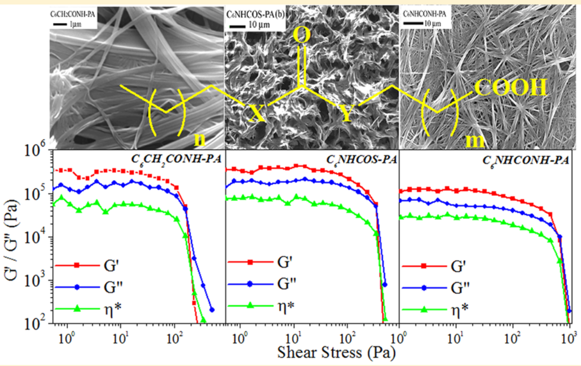
Supporting Information

ABSTRACT: In this work, we have designed and synthesized a series of fatty acid amphiphiles that have the same structural skeleton but different hydrogen-bonding (H-bonding) functional groups in the hydrocarbon chain. To examine the importance of the H-bonding interaction on the formation of a one-dimensional (1D) aggregate in organic solvents, we have compared the gelation behavior of these amphiphiles in some common organic solvents at room temperature. Despite the structural similarity, the amphiphiles were observed to exhibit different gelation behavior. The organogels were characterized using conventional techniques such as field emission scanning electron microscopy, X-ray diffraction, and rheology. A systematic analysis of the FT-IR and ^{1}H NMR spectral data, gel melting temperatures, and mechanical strengths of the organogels in a given solvent suggested the importance of H-bonding as well as van der Waals interaction in the gelation process. In this study, we have made an attempt to estimate qualitatively the relative contribution of H-bonding and van der Waals interactions between gelator molecules forming organogels. The results suggest that strong and weaker H-bonding affects the gelation ability of gelators. However, when the H-bonding interaction is weak, an increase in van der Waals interactions can result in gelation, but when both H-bonding and van der Waals interactions are weak, that is, when the amphiphiles are liquid and semisolid, no gelation is observed. It is concluded that a balance between H-bonding and van der Waals interactions is necessary for physical gelation.



1. INTRODUCTION

In the recent literature, the physical gelation of liquids by low-molecular-weight gelators (LMWGs) has been studied with a great deal of interest owing to their impacts in various fields including molecular self-assembly (SA), smart materials, and controlled drug release.[1−13] Over the last three decades, many LMWGs with excellent gelation abilities have been reported. These include steroids, amide-[14−18] and urea-type[19−21] compounds, sugar amphiphiles,[22−25] and so forth. Most of these gelators, however, were discovered by accident. These gelators form gels via platelets, colloids, or the formation of a network of fibers as a compromised result of weak noncovalent interactions (e.g., ion−ion, H-bonding, $\pi-\pi$ stacking, van der Waals (vdW), etc.). It is believed that in the case of the latter that form a self-assembled fibrillar network (SAFIN), the anisotropy of the intermolecular interaction is essential to the growth of aggregates in one dimension (1D). Although there are numerous examples of organogelators, the weak intermolecular forces that dominate physical gelation are not properly understood. However, understanding the mechanism of gelation by LMWGs is essential to designing new gelator molecules.

The LMWGs reported in the literature fall into two major classes, hydrogen-bond- and non-hydrogen-bond-type gelators. The H-bonding interaction is responsible for the gelation of organic liquids by amide compounds such as amino acids[14−18] and urea[19−21] and by hydroxyl compounds such as sugars.[22−25] However, anthracene, cholesterol, and tropone derivatives[26−30] are non-hydrogen-bond-based gelators. In fact, in most cases of organogelation, it was observed that H-bonding is the dominant factor. Previously it was reported that *N*-alkanoyl-L-alanine amphiphiles gelate a series of organic solvents[31,32] in which the driving force for the gelation process was the amide H-bonding between two adjacent molecules. Generally, H-bonding networks are destroyed by the addition of a small amount of H-bonding additives, such as water, methanol, urea, thiourea, and so forth, resulting in a disruption of the gel structure. In contrast, we have reported some amino acid-based gelators containing a urea linkage that produced organogels in the presence of a critical amount of H-bonding additives.[33] The same gelators, however, failed to gelate organic liquids in the presence of tetrabutylammonium fluoride (TBAF), which is known to be a strong H-bond breaker. This means that when H-bonds are completely broken, the gel structure is destroyed.

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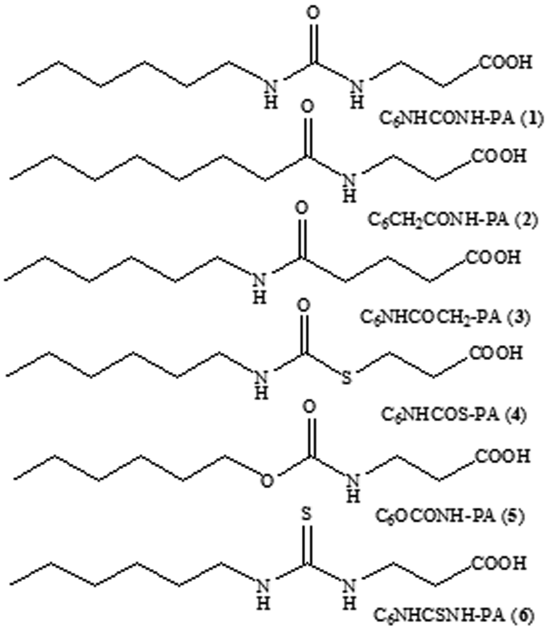
In other words, relatively weak H-bonding favors gelation but a stronger H-bonding interaction between gelator molecules leads to poor solubility or crystallization of the gelator on cooling.

In the present work, an extension of our previous study, we have designed and synthesized a series of amphiphilic molecules with the same structural skeleton but having different H-bonding groups in the hydrocarbon chain in order to investigate the relative importance of H-bonding and vdW interactions between gelator molecules on physical gelation. The chemical structures of the amphiphiles (**1**−**6**) are shown in Chart 1. As can be seen, the amphiphiles contain a urea (−NHCONH−), amide (−CH_2CONH− and −NHCOCH_2−), sulfonamide (−NHCOS−), thiourea (−NHCSNH−), or urethane (−OCONH−) linkage, all of which have different H-bonding strengths. However, all of the amphiphiles have the same hydrocarbon chain lengths (C_6), which ensure similar vdW interactions between hydrocarbon tails. To compensate for the weak H-bonding interaction in the case of amphiphiles **3** and **5**, we have also synthesized their longer-chain analogs **3a** and **5a** containing a C_{12} hydrocarbon tail and **5b** containing a C_{14} hydrocarbon tail that can have greater vdW interactions. The gelation behavior of these amphiphiles was studied and compared in common organic solvents. The critical gelation concentration (CGC) and gel-to-sol transition temperature (T_{gs}) of the organogels were compared. The morphology of the organogels was studied by field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The viscoelastic behavior was also compared among gels. ^{1}H NMR and FT-IR spectroscopy were used to study the mechanism of gelation.

Chart 1. Chemical Structure of the Amphiphiles



2. EXPERIMENTAL SECTION

2.1. Materials. Triethylamine (TEA), *n*-hexanol, glutaric anhydride, hexyl amine, *o*-xylene (*o*-Ph$(Me)_2$), *m*-xylene (*m*-Ph$(Me)_2$), *p*-xylene (*p*-Ph$(Me)_2$), benzene (PhH), toluene (PhMe), chlorobenzene (PhCl), and nitrobenzene (Ph(NO_2) were purchased from SRL (Mumbai, India) and were used without further purification. Chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) were purchased from Merck, Mumbai, India. β-Alanine (3-amino propionic acid), 3-mercapto propionic acid, 4-nitrophenyl chloroformate, octanoyl chloride, hexyl isothiocyanate, mesitylene (Ph$(Me)_3$), and hexyl isocyanate were obtained from Sigma-Aldrich (Bangalore, India). All other organic solvents were of the highest purity commercially available and were dried and freshly distilled before use. The amphiphiles employed in this study were synthesized in the laboratory following literature reported methods. The details of syntheses and chemical identifications are described in the Supporting Information (SI).

2.2. Methods and Instrumentation. The FT-IR spectra were recorded with a PerkinElmer (model Spectrum Rx I) spectrometer. The ^{1}H NMR spectra were recorded on a Bruker AVANCE DAX-400 (Bruker, Sweden) 400 MHz instrument in $CDCl_3$ or CD_3OD solvent with TMS as a reference standard. Melting-point measurements were carried out using an Instind (Kolkata) melting-point apparatus with open capillaries. All measurements were performed at room temperature (∼303 K) unless otherwise mentioned.

The gelation abilities of the amphiphiles were estimated in terms of the CGC, which is defined as the minimum concentration of gelator required to gelate a certain amount of solvent at a certain temperature. Gelation was studied by dissolving 5 mg of a solid gelator in a screw-capped vial in the requisite volume of organic solvent by heating in a hot water bath (∼50−80 °C per the solvent's boiling point), followed by cooling at 298 K in a temperature-controlled water bath (Julabo, model F12). The gelation was confirmed by flow in the inversion test method; it was considered to be a gel when the material did not flow due to gravity upon inversion of the vial.

The thermal stability of the organogels was measured by determining the gel-to-sol transition temperature (T_{gs}), which is defined as the temperature at which the gel is transformed into the solution (sol). The T_{gs} values of the organogels were determined by an inverted-tube experiment in which the screw-capped vial containing the gel was put in a temperature-controlled water bath (Julabo, model F12). The temperature of the bath was gradually increased at a rate of 1 °C/min, and the temperature was noted where the gelated mass started to flow on tilting of the vial. Each experiment was repeated at least twice. When the melting temperature did not vary more than ±1 °C, it was recorded as T_{gs}.

For the measurement of morphology, a hot sample of a solution was placed on the aluminum foil and allowed to cool at room temperature. The specimen after drying in desiccators was coated with gold particles to make the conducting surface and finally transferred to the field emission scanning electron microscope (FESEM, Zeiss, Supra-40) operating at 5−10 kV to get the micrograph.

For XRD measurements, the organogel was placed on a glass slide and allowed to dry in air for 2 days and then in desiccators for 1 day at room temperature. The experiments were carried out on an X-ray diffractometer (Pan Analytical (PW 3040/60), X'pert PRO, The Netherlands) using Ni-filtered Cu Kα (154.05 pm) radiation. The instrument was operated at a voltage of 40 kV and a current of 30 mA. The spectrum was recorded at room temperature between 2 and 12° in the 2θ scan mode in steps of 0.02° in 2θ at a scan speed of 0.001 s^{-1}.

The rheological measurements in flow and oscillatory mode were carried out in a 20-mm-diameter parallel plate configuration with a solvent trap and a gap of 100 μm using a Bohlin RS D-100 (Malvern, U.K.) rheometer. The Peltier plate on which the sample was kept had a temperature of 298 ± 0.1 K. An equilibration time of 30 min was allowed before taking measurements for each sample. All measurements were taken on matured gels after 10 h of cooling. The samples were loaded onto the rheometer plate as gels. The gels were made in a wide-mouthed capped vial and were easily scooped out by use of a spatula without causing any damage to the gel structure. For flow measurements (viscosity), the gels were subjected to a preshear at 20 s^{-1} for 1 min, followed by equilibration for 3 min. Oscillatory stress sweeps from 1 to 1000 Pa were measured at a constant frequency of 1 Hz to obtain the storage modulus (G') and loss modulus (G''). The frequency sweep measurements were performed in the frequency range from 0.01 to 100 Hz (or 40 Hz) at a constant stress in the linear viscoelastic regime as obtained from the stress sweep measurement of each gelator.

3. RESULTS

3.1. Gelation Behavior. The gelation behaviors of all of the amphiphiles studied in different organic solvents are summarized in Table 1. Among the amphiphiles examined here, amphiphile **5** with a urethane linkage (−OCONH−) is a liquid and amphiphile **6** with a thiourea (−NHCSNH−) linkage is a semisolid. Because liquids are normally nongelators because of weak intermolecular forces, amphiphiles **5** and **6** did not exhibit any gelation in any of the solvents employed. It is surprising to observe that despite all of the amphiphiles having the same hydrocarbon chain length (C_6) and the same headgroup (−COOH), they exhibit different gelation abilities in the organic solvents employed in this work. Amphiphile **3** remained soluble in all of the solvents up to a very high concentration. Though **3** failed to gelate organic solvents, **3a** with a longer chain length (C_{12}) gelated organic solvents but with relatively higher values of CGC. Although both **3a** and **5a** have the same hydrocarbon chain length (C_{12}), the latter was found to be a semisolid at room temperature because of the relatively free rotation of the hydrocarbon chain around C−O compared to that around the C−C bond. Therefore, as expected, **5a** did not produce gel in any of the solvents employed. However, amphiphile **5b** with a C_{14} chain was obtained as solid and could gelate the organic liquids at a much lower concentration than could **3a**. It should be noted that none of these amphiphiles, except **1**, formed gel in H-bond donor solvents, such as chloroform. Amphiphile **1** remained insoluble even on heating. However, on addition of a small amount of H_2O, the amphiphile dissolved on warming the organic solvent, which on cooling turned into gel with a CGC value of <2% (w/v). A similar phenomenon has already been reported by us.[33] The data in Table 1 show that amphiphiles **2** and **4** gelate most of the aromatic solvents employed without the addition of H_2O but the gelation ability of **4** increased when a small amount of H_2O was added. In contrast, the organogels formed by **2** break down upon addition of H_2O.

Table 1. Gelation Behavior and the CGC (±0.1% w/v) Values of Gelators 1, 2, 3, 3a, 4, 5, 5b, and 6 at 298 K[a,b]

solvent	1	2	3	3a	4	5	5b	6
$CHCl_3$	I (1.1)	S	S	S	S	S		S
CCl_4		P	S		P	S		I
PhH	I (0.9)	P	S	4.8	6.1 (3.1)	S	1.5	I
PhMe	I (0.9)	2.6	S	4.9	6.3 (3.1)	S	1.4	I
o-Ph(Me)$_2$	I (1.0)	3.1	S	3.9	3.3 (2.2)	S	1.4	I
m-Ph(Me)$_2$	I (0.9)	2.0	S	3.5	3.0 (2.0)	S	1.1	I
	47	*30*					*43*	
p-Ph(Me)$_2$	I (0.8)	2.6	S	3.7	3.6 (2.5)	S	1.3	I
	52	*27*					*41*	
Ph(Me)$_3$	I (1.1)	1.4	S	4.6	3.5 (2.3)	S	0.9	I
PhCl	I (1.8)	P	S	6.0	6.6 (5.6)	S	1.8	S
$PhNO_2$	I (1.7)	P	S	4.6	Cy	S	1.3	S

[a] I, insoluble; S, soluble; P, precipitation; Cy, crystallization. [b] The values in parentheses represent CGC values in the presence of H_2O (50 mol/mol gelator) at 298 K. The values in italics represent the corresponding T_{gs} values in °C at a gelator concentration of 0.05 M.

Although both **2** and **3** amphiphiles have amide linkages, the vdW interaction in the former molecule is slightly higher than that in the latter. This is evidenced by the slightly higher melting point (96−98 °C) of **2** compared to that of **3** (86−88 °C). The later molecule has one less $-CH_2-$ in the hydrocarbon chain. The structural difference between the two amphiphiles is only in the position of the amide group. The former amphiphile gelates some organic solvents but the later remains soluble in all of the organic solvents employed for the gelation test. This might be due to the difference in molecular conformation around the amide group of the gelators which inhibits the H-bonding interaction between −NHCO− groups of the adjacent molecules. However, it is reported that the higher homologue of **2** is a better gelator, indicating the role of a greater vdW interaction in the self-assembly formation.[34] For the same reason, **3a**, the higher homologue of **3**, also gelates organic solvent. Thus, it can be concluded that though H-bonding plays a major role in organogelation, the effect of H-bonding can be compensated for to some extent by vdW interactions.

To investigate the effect of solvents on the efficacy of gelation, the CGC values of respective gelators were correlated with different polarity parameters, such as the dielectric constant (ε) and Kamlet−Taft solvatochromic parameters.[35] The latter includes a generalized polarity parameter (π^*) and hydrogen-bond-donating (α) and -accepting (β) parameters.[35] The dielectric constants and Kamlet−Taft solvatochromic parameters related to the series of solvents employed in this work are listed in Table S1. The plots of the respective CGC values of gelators **1**, **2**, **3a**, **4**, and **5b** in non-hydrogen-bonding solvents as a function of the dielectric constant (ε) and generalized polarity parameter (π^*) are presented in Figure S1 of the SI. The analysis of the results clearly suggests that there is no significant correlation between the gelation abilities of the amphiphiles and the dielectric constant or generalized polarity parameter (π^*).

3.2. Morphology of the Organogels. The supramolecular structures in the organogels produced by the gelators were obtained from FESEM measurements. Figure 1 exhibits FESEM images of the air-dried organogels in *p*-Ph(Me)$_2$. As observed, the morphology of the organogels can be characterized by ribbonlike fibrous aggregates with a high aspect ratio, forming three-dimensional (3D) networks in the cases of **1** and **2**. In contrast, gelator **4** forms paperlike flat two-dimensional (2D) lamellar structures with a low aspect ratio under both conditions. The lamellar structures of the **4** organogel become thicker when the gel is prepared in the presence of water. Among all of the amphiphiles, the organogel of **1** exhibits maximum cross-linking in its network structure and the fibers of the network structure are also very thick. The fibers formed in the organogel of **2** are continuous, but there is less cross-linking among the fibers than in the case of **1**. The denser intertwined fibrous structure of the organogels of **1** reflects greater intermolecular cohesiveness and hence higher thermal (which means higher T_{gs} value) and mechanical stability (i.e., greater σ_y values). However, the small 2D lamellar structures in the case of **4** show no cross-linking, which is indicative of weak gels.

In support of the structures shown by the FESEM images of the organogels, we have performed XRD measurements using respective air-dried gels. The XRD spectra of the organogels in *p*-Ph(Me)$_2$ solvent are shown in Figure 2. The periodicity of the reflection peaks in the XRD spectra clearly indicates the

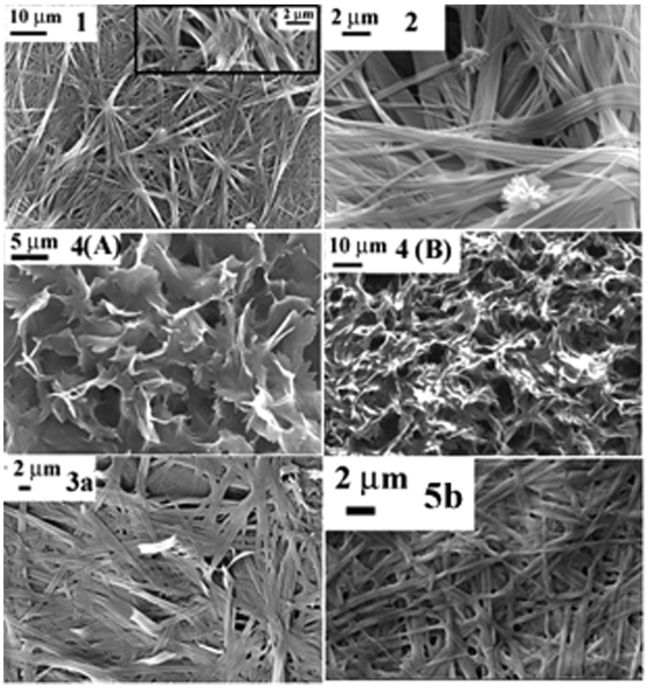


Figure 1. FESEM images of the air-dried organogels of **1**, **2**, **4**, **3a**, and **5b** organogels in *p*-Ph(Me)$_2$ at 0.05M. **4**(A) and **4**(B) represent FESEM images of gels formed in the absence and presence of H_2O, respectively.

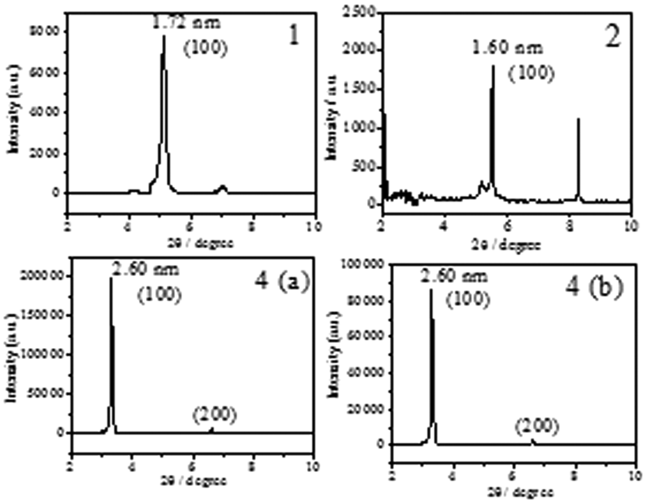


Figure 2. XRD spectra of the air-dried organogels of **1**, **2**, and **4** in *p*-Ph(Me)$_2$ at 25 °C. **4** (a) and **4** (b) represent the gel made in the presence and absence of H_2O, respectively.

presence of bilayer lamellar structures. The bilayer thicknesses can be taken to be equal to the interlayer distance (*d*) of 100 planes. The *d* values obtained for **1**, **2**, and **4** are 1.72, 1.60, and 2.60 nm, respectively. The bilayer thickness was found to be either smaller or almost equal to twice the extended chain length of the hydrocarbon tail (1.22, 1.25, and 1.30 nm for **1**, **2**, and **4**, respectively)[36] of the gelator molecules. In agreement with the FESEM images, the XRD data of the xerogel of **4** in the presence and absence of water appear to be similar.

3.3. Thermal Stability. The thermal stability of the organogels was measured by determining the gel-to-sol transition temperature (T_{gs}) at 0.05 M gelator concentration. Gelators **3a** and **4** could not gelate any organic solvents at this concentration because they have higher CGC values. The T_{gs} values of the gels formed by gelators **1**, **2**, and **5b** were determined in *p*-Ph(Me)$_2$ and *m*-Ph(Me)$_2$ solvents, and the respective data are included in Table 1. The T_{gs} value of all of the gelators in both the solvents decreases in the order **1** > **5b** > **2**. Therefore, the gels formed by gelator **1** have the highest T_{gs} value indicating the highest thermal stability of all gels, which is consistent with the highest gelation capacity, i.e., lowest CGC values of the gelator.

3.4. Viscoelastic Behavior. In *m*-Ph(Me)$_2$ solvent, the gelation ability of all of the gelators is optimum, as indicated by the lowest CGC value. Among all of the amphiphiles, **2**, **3a**, and **4** produced weak organogels at 0.05 M concentration in pure solvents. However, as mentioned earlier, the organogels of **4** become stronger upon addition of a small amount of H_2O. Therefore, in the cases of gelators **1** and **4**, the viscoelastic properties of the organogels (0.05 M) produced by adding H_2O were measured. On the other hand, the mechanical strength of the **5b** organogel in pure *m*-Ph(Me)$_2$ solvent was measured and compared with those of **1**, **2**, and **4**.

The mechanical strength of a gel is a function of the gelator concentration and is measured by the storage modulus (G') and loss modulus (G''). These quantities were measured as a function of applied stress (σ) and frequency (f) using organogels with a gelator concentration of 0.105 M in *m*-Ph(Me)$_2$ solvent. Figure 3 shows the variation of G' and G'' with frequency. It is observed that in all cases both G' and G'' are almost independent of frequency, confirming the gel structure. Also, at any given frequency G' is much higher than G'', indicating the elastic nature. Figure 4 shows the plots of G' and G'' versus applied shear stress (σ) at a constant frequency of 1 Hz. It can be observed that up to a critical stress value, usually called the yield stress (σ_y), G' has a greater value than G'', but above that value both G' and G'' abruptly fall to a very low value, and in this region G'' has a greater value than G', indicating the flow of the organogel. The variation of G' and G'' values of **5b** has also been measured as a function of frequency and shear stress and is shown in Figures 3 and 4, respectively. The σ_y values of **1**, **4**, **2**, and **5b** are 475, 234, 110, and 41 Pa, respectively. According to the σ_y values, the organogel of **1** is the strongest and that of **2** is the weakest. The increased mechanical stability of the organogels of **1** and **4** in the

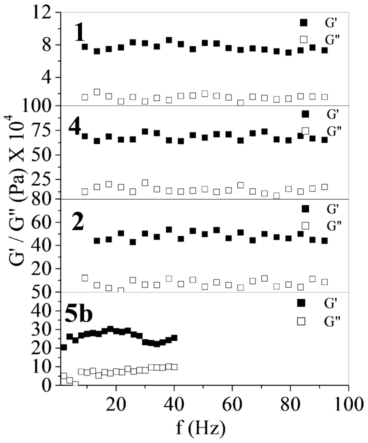


Figure 3. Variation of the storage modulus (G') and loss modulus (G'') of the **1**, **2**, **4**, and **5b** organogels in *m*-Ph(Me)$_2$ with frequency (f) at 298 K.

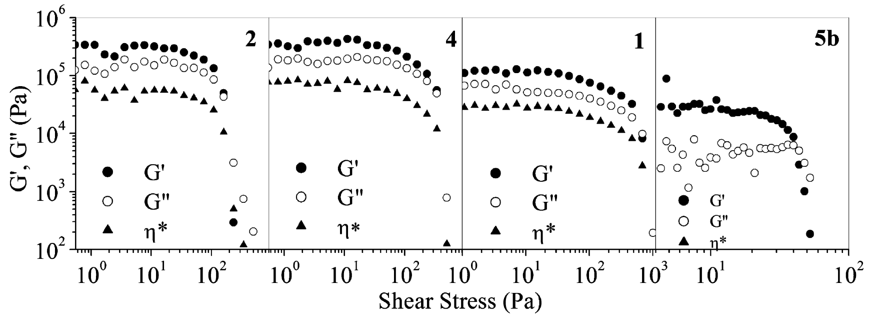


Figure 4. Variation of the storage modulus (G') and loss modulus (G'') of the **1**, **2**, **4**, and **5b** organogels in *m*-Ph(Me)$_2$ with shear stress at 298 K.

Table 2. FT-IR Data (cm^{-1}) of Amphiphiles 1–6[a]

	ν (cm^{-1})					
type	**1**	**2**	**3**	**4**	**5**	**6**
amide A	3318 (3317)	3357	3358	3320 (3321) 3322	3355	3385
amide I or C═S	1635 (1611)	1684	1685	1638 (1638) 1640	1640	740
amide II	1578 (1570)	1569	1570	1520 (1521) 1522	1532	1570
C═O of (COOH)	1694 (1693)	1715	1715	1686 (1692) 1693	1687	1695

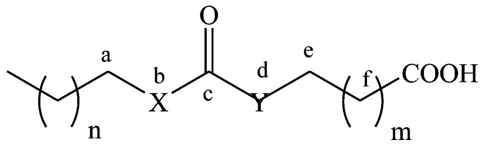
[a] Data within parentheses correspond to the gel state in the presence of H_2O, and the data given in italics refer to the values in a 0.01 M solution of $CHCl_3$.

presence of H_2O might be due to the growth of 1D (or 2D) aggregates as a result of H_2O-mediated intermolecular H-bonding interactions.

4. DISCUSSION

Amphiphiles **1**–**6** have the same structural skeleton; that is, all of them have a long alkyl chain containing an H-bonding group and a −COOH headgroup. However, the H-bonding strengths of these groups are different. Basically, the H-bonding strength increases with the increase in the number of functional group having atoms with higher electronegativity. Resonance also plays a role in the H-bond formation, with the extent of H-bonding decreasing if there is resonance in a functional group (e.g., −OCONH−). Thus, in these molecules, the H-bonding strength decreases in the order −NHCONH− (**1**) > −CH$_2$CONH− (**2**, **3**) > −SCONH− (**4**) > −NHCSNH− (**6**) > −OCONH− (**5**). Accordingly, gelator **1** is expected to be more active in aggregation. The NH group in a thiourea is more acidic than in the corresponding urea, but the urea derivative has greater ability to aggregate because ureas are stronger bases. The acidity of the NH groups does not appear to play any role in aggregation. This is also supported by theoretical calculations, which show that the interaction angles involving electron lone pairs are narrower in the urea derivatives, which favors the formation of linear aggregates.[37] Linear forms of aggregation lead to an increase in the dipole moment with an increase in concentration. In contrast, for monoalkyl derivatives of thioureas, the dipole moment decreases because branched aggregation is observed with thioureas. Consequently, **6** is a nongelator. However, some change in donor−acceptor interactions may result as the number of proton donor (N−H) groups changes. Indeed, linear aggregate formation abilities of the urethane, amides, and sulfonamides are much less than that of the urea derivative (**1**). This is indicated by the CGC values in Table 1. The H-bonding strength of the linker groups is further reflected in their solid melting-point (T_m) values that decrease in the order **1** > **2** > **4** > **3** > **6** > **5**. It is generally observed that solid compounds with a higher melting temperature form gels. Consequently, **1**, **2**, and **4** with greater H-bonding interactions and hence greater melting points gelate organic liquids. This implies that only compounds with strong intermolecular interactions can form gels. In fact, previously we

Table 3. Dihedral Angles of Amphiphiles 1–6



amphiphiles	dihedral angles (X^{b}C^{c}Y^{d}C^e)
1	170.60
2	175.87
3	167.30
3a	179.85
4	170.03
5	−177.26
5b	−178.90
6	170.41

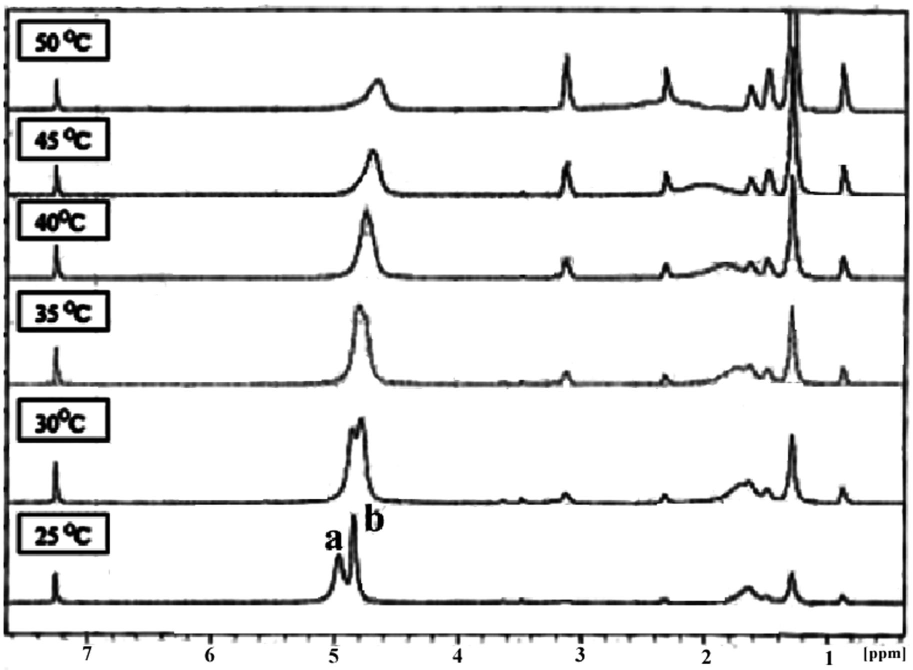


Figure 5. ^{1}H NMR spectra of organogel **1** in $CDCl_3$ containing H_2O at different temperatures. Peak a represents H_2O bound to the urea group, and peak b represents H_2O trapped in the bilayer.

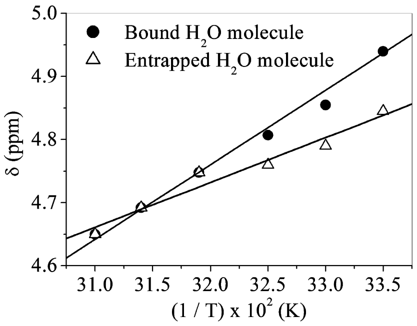


Figure 6. Variation of the chemical shift (δ/ppm) of H_2O with temperature (T/K) in the ^{1}H NMR spectra of the $CDCl_3$ organogel of **1**.

have shown that the longer-chain homologues of **2** are better gelators because of the increased vdW interaction in the self-assembly.[33] This is also shown by the gelation ability of **3a**, which has a longer hydrocarbon (C_{12}) tail. The same behavior is further observed with **5b** having a C_{14} chain. A longer hydrocarbon tail means greater vdW interactions that compensate for the weaker H-bonds in amphiphiles **3** and **5**. Interestingly, although amphiphiles **2** and **3** have an amide group in the hydrocarbon chain, the latter has a T_m value less than that of the former. The FT-IR spectral data (Table 2) of the solid samples also show that the H-bonding strengths of the amphiphiles are expected to be similar. Therefore, the difference in solid melting points and gelation abilities might be due to the difference in molecular conformation, which along with intermolecular interactions dictates molecular packing in the crystal.

In the case of amphiphile **1**, the amide A (N−H stretching), amide I (C=O stretching) and amide II (N−H bending) stretching frequencies are much more red-shifted compared to those of **2**, **4**, or **3**, indicating strong H-bonding between urea groups in the solid state. The corresponding dihedral angles also suggest that amphiphile **1** has a linear conformation causing tight packing in the crystal. Thus, **1** is insoluble in almost all of the organic solvents employed in the gelation study, even on warming resulting from the strong intermolecular interactions and tight packing as indicated by its higher T_m value. Upon addition of H-bonding additives such as H_2O and MeOH, the relatively stronger intermolecular H-bonds between the amphiphile and the additive molecules result in weakening of the intermolecular H-bonding between urea groups of adjacent gelator molecules. Thus, the amphiphile becomes soluble on warming and forms a gel on cooling. To investigate the state of H-bonding in the gel state, the FT-IR spectrum of the *p*-Ph(Me)$_2$ organogel of **1** was recorded. It can be observed that the amide I and amide II stretching frequencies are more red-shifted compared to the corresponding value in the powder state (Table 2). This means that in the gel state the gelator molecule forms stronger H-bonds with the additive molecule. The H-bonding additives partially break the intermolecular H-bonds and facilitate gelation.

To examine their molecular conformations, we have calculated the dihedral angles (Table 3) around the amide group in the hydrocarbon chain. Though amphiphile **6** has a dihedral angle greater than 170°, indicating a flatter structure than the other amphiphiles, the electronegativity of the S atom is not large enough to form H-bonds. The low dihedral angle (167°) of **3** in comparison to that of **2** (175°) suggests that the latter molecule is almost linear but amphiphile **3** has a slightly bent structure, preventing tight packing of the molecules in the crystal. The same is also true in the self-assembled structures in the organogel state and explains the failure to gelate organic liquids by amphiphile **3**. However, in the cases of gelators **3a** and **5b**, the increased vdW interactions due to the longer hydrocarbon tail causes tight packing and hence gelation. Thus, it can be concluded that in the self-assembly formation, weak H-bonding interactions can be compensated for by the equivalent increase in vdW interactions.

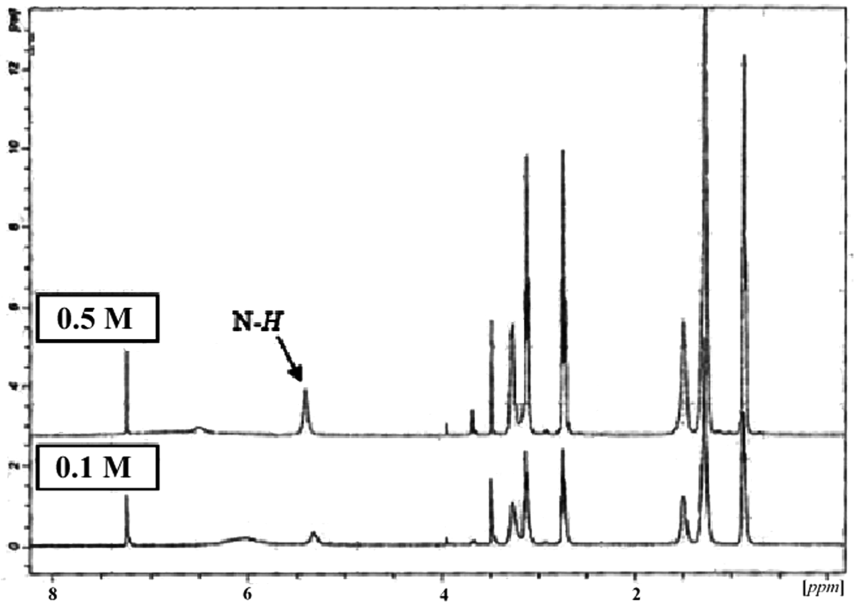


Figure 7. ^{1}H NMR of **4** in $CDCl_3$ at different concentrations.

The role of H_2O in the gelation process may be understood by the variable temperature ^{1}H NMR spectra of the $CDCl_3$ organogel of **1** presented in Figure 5. It can be observed that at low temperatures, the peak ($\delta \sim 4.6$-4.9 ppm) due to the H_2O molecule is split in to two peaks which gradually merge into one with the rise in temperature. This indicates that at low temperature, in the gel state, the H_2O molecules exist in two different forms, (a) H_2O molecules that are bound to the urea group and (b) H_2O molecules that are entrapped between the bilayer. With the increase in temperature, the gel breaks, both kinds of H_2O molecules become free, and the NMR spectrum shows only one peak. Interestingly, both peaks appeared again when the sample was cooled to form the gel (Figure S2). Similar behavior was also observed with a structurally similar urea amphiphile in our earlier paper.[33] A significant downfield shift of the chemical shift position of both types of H_2O molecules from 4.65 ppm at 323 K to 4.96 and 4.85 ppm at 298 K clearly indicates H-bond formation between the H_2O molecule and urea group of the amphiphile in the gel state. The plot of the variation of δ with temperature is shown in Figure 6. The plot exhibits a linear decrease in δ with the increase in temperature.

In the case of gelator **4**, H-bonding also plays a similar role as in **1**, but the extent of H-bonding is weaker in this amphiphile, which is indicated by the low T_m value. As a result, the amphiphile becomes more soluble in the organic solvents on heating and forms a gel on cooling. But the gelation efficiency increased upon addition of H_2O, an H-bonding additive. The red shift of the FT-IR bands in dilute (0.01 M) solution (data in Table 2) in $CHCl_3$ confirms the presence of H-bonds in the solid compound. The H-bonding between the −NHCOS− groups in the gel state of **4** is confirmed by the FT-IR data in Table 2. It is observed that the stretching frequencies are exactly similar to the corresponding frequencies in the solid state. The ^{1}H NMR spectra (Figure 7) in $CDCl_3$ solvent also show that the amide N−H peak shifts from 5.32 to 5.41 ppm in going from 0.1 to 0.5 M concentration. This downfield shifting of the N−H proton at the high concentration suggests an H-bonding interaction in the gel state.

5. CONCLUSIONS

The gelation behavior of a series of amphiphiles that bear a six-carbon-containing aliphatic chain linked to the propionic acid moiety via an H-bonding group has been reported. Among these amphiphiles, **3**, **5**, and **6** do not show gelation in any solvent employed whereas **1**, **2**, and **4** produce gels. However, when the hydrocarbon chain length of **3** and **5** is increased, the resulting amphiphiles become good gelators. The main driving force for this gelation is the H-bonding interaction as evidenced by the FT-IR and ^{1}H NMR data. Stronger H-bonding interactions result in stronger organogels. The thermal stability and rheological behavior showed that thick, long fibers of the assembly that cause more entanglement in the network structure result in better gelation in the cases of amide and urea derivatives. In contrast, weaker H-bonding results in flat lamellar structures with a low aspect ratio, causing the organogel to be mechanically less stable.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and chemical identification of the amphiphiles and rheological measurement of the $C_{14}OCONH$-PA organogels in *m*-Ph(Me)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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