Concentration- and Temperature-Responsive Reversible Transition in Amide-Functionalized Surface-Active Ionic Liquids: Micelles to Vesicles to Organogel

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ABSTRACT: A ubiquitous example of DNA and proteins inspires the scientific community to design synthetic systems that can construct various self-assembled complex nano-objects for high-end physiological functions. To gain insight into judiciously designed artificial amphiphilic structures that through self-assembling form various morphological architectures within a single system, herein, we have studied self-aggregation of amide-functionalized surface-active ionic liquids (AFSAILs) with different head groups in the DMSO/water mixed system. The AFSAIL forms stimuli-responsive reversible micelle and vesicle configurations that coexist with three-dimensional (3D) network structures, the organogel in the DMSO/water mixed system. The self-assembly driving forces, self-organization patterns, network morphologies, and mechanical properties of these network structures have been investigated. With the proven biodegradability and biocompatibility, one can envisage these AFSAILs as the molecules with a new dimension of versatility.

INTRODUCTION

Self-assembled artificial network structures that can compete with the natural systems such as DNA and proteins in their complexity and functionality are yet to be constructed. Strategically designed amphiphiles that can form various structural architectures including three-dimensional (3D) network structures, that is, gels, make an exciting bottom-up approach for fabricating nano- and microstructured materials with advanced functional properties. These supramolecular structures have attracted significant attention in various fields including food, cosmetics, removal of toxic pollutants, vehicles for drug delivery, biomimelerization, templates to synthesis nanomaterials, as chem- and biosensors, in solar cells, as catalysts, as scaffolds for tissue engineering, in enzyme immobilization, as optical and electronic components for wearable devices, and oil spill recovery to cite few. These supramolecular structures are formed as a result of various noncovalent interactions including hydrogen bonding, π–π stacking, and van der Waals interactions. These noncovalent interactions and so the network structure could be rationally designed through judicious selection of various building blocks and through placing them under external stimuli such as pH, temperature, light, solvents, magnetic field, metal ions, and others. Among the spectrum of available surfactants, ionic surfactants have edge over others because of their ability to form well-organized discrete nano- and microaggregates such as vesicles, wormlike micelles, microtubes, lamellar sheets, and 3D fibrous gels within a single system through ease and their ability to sequester a range of molecules including biological and pharmaceutical ones that can mimic the natural systems. In an attempt to have novel surfactant structures that have ionic liquid (IL) character, the better known as surface-active ionic liquids (SAILs) are studied for their formation behavior in an aqueous medium. Traditional surfactants, although having similar molecular architectures to 10–15 ILs, do not fit in this category because of their higher melting points (>100 °C). Several groups including our own group have reported the formation of various structural architectures, viz., micelles, wormlike micelles, lamellar, vesicles, coacervates, and gels through (i) self-assembling of these SAILs in aqueous and nonaqueous media, (ii) synergistic interactions of SAILs with various additives, and (iii) stimuli response. Among these, solvent-induced aggregation is interesting as it is controlled by a delicate balance of various noncovalent interactions as stated above. Self-aggregation in these system...
leads to the formation of various 1D arrays such as micelles and vesicles that through topological entanglement at higher concentrations leads to the formation of 3D soft semisolid-like material also known as organogels.5,6,28,29 The properties and the morphologies of these organogels could be tailored through changing the solvent conditions, that is, polarity, dielectric constant, concentration, and pH for the same SAIL or through the SAIL with a slightly modified structure for the same solvent. Because of their characteristic stimuli-responsive properties, they have found applications in diverse fields and are included in the group of smart materials.30–32

Pursuant to continued research in designing SAILs with tailor-made properties including functionalized SAILs, herein, we had studied aggregation behavior of three amide-functionalized SAILs (AFSAILs) with the same terminal long alkyl side chain (C16) and different head groups (imidazolium, morpholinium, and pyridinium) (Figure 1) in the DMSO/water binary mixture. The AFSAILs used here are 4-methyl-4-(2-((hexadecylamino)-2-oxoethyl)morpholin-4-ium bromide (C16AMorphBr), 3-((hexadecylamino)-2-oxoethyl)-1-methyl-1H-imidazole-3-ium bromide (C16AMeImBr), and 1-((hexadecylamino)-2-oxoethyl)-1-methylpyridin-1-ium bromide (C16APyBr). These AFSAILs exhibited unprecedented reversible aggregation behavior through the transformation of spherically shaped micellar aggregates into vesicles and then organogels (Figure 1) beyond their respective critical gelation concentrations (CGC). Introducing an amide functionality such as in the case of carboxylic, hydroxyl, ester, and ether within the alkyl chain close to the hydrophilic head group increases biodegradability and biocompatibility, making them better choices against their nonfunctionalized and traditional analogues surfactants.33,34 Because of the intermolecular hydrogen bonding within the AFSAILs, the organization of molecules in the AFSAILs is affected, which substantially improves the thermal stabilities than their ester-functionalized counterparts.33,34 The amide group that is in the vicinity to the head group along with the long alkyl chain (C16) provides flexibility, decreases the counterion binding, and exposes the amide group to water that leads to higher hydration of the head group as compared to its lower alkyl chain counterparts, that is, C8 and C12.34 Self-assembling behavior leading to the formation of distinct micellar structures of C16AMorphBr has been reported. Transformation of the aggregated structures with concentration is yet to be investigated and is one of the prime objectives of this work. Among the range of self-organized structures within the single amphiphilic system, vesicles, because of their special bilayer structures, can mimic the biological membranes.35 Furthermore, vesicles prepared from the cationic surfactants are superior than the nonionic surfactant-based niosomes and lipid-based liposomes because of their simple formulation, chemical stability against hydrolyses, and oxidative degradation in aqueous media and their ability to sequester a range of functional molecules irrespective of their charge, size, and shape.36,37 However, 3D network structures, the gels, because of their unique physicochemical properties, exhibited application in diverse fields from biomedical to electronics. In this work, we have studied the stimuli-responsive morphological structures including vesicles and gels within a single system in the DMSO/water system. Nevertheless, despite the extensive literature on the self-assembly behavior of SAILs in aqueous solution, the research on binary mixtures and that too on the transformation of stimuli-responsive aggregated structures is unavailable.

### RESULTS AND DISCUSSION

#### Rationale for the Effect of DMSO on the Micellar Properties of AFSAILs

In the present work, micellization of three AFSAILs, C16AMorphBr, C16AMeImBr, and C16APyBr, has been studied in two different solvent systems, (1) in water and (2) in the binary solvent system of DMSO/water (1:3 v/v). Studied AFSAILs have limited solubility in water, that is, C16AMeImBr, C16AMorphBr, and C16APyBr are soluble up to 2.25, 1.72, and 2.26 mM, respectively, in water. It has been observed that all the three ILs are freely soluble in polar apotic solvents such as DMSO and DMF, whereas they are soluble in hot alcohols (~50–55 °C) at and beyond their CGCs. At the selected ratio of study (1:3, DMSO/water), all AFSAILs form clear isotropic solution at and beyond the CGC, that is, 21 mM (10 mg/mL), 27 mM (12 mg/mL), and 31 mM (14 mg/mL) for C16AMorphBr, C16AMeImBr, and C16APyBr at room temperature (RT), respectively. AFSAILs studied herein have identical tails and functionality, but they differ in their head groups, promoting different levels of interfacial and micellar properties in general.

We used surface tension measurement as the tool to investigate the self-assembly in an aqueous medium and found that the cmc obtained is in good agreement with the reported literature (Table 1).34 Herein, hydrophobicity of the head group plays a dominant role in deciding cmc; imidazolium and pyridinium heads having higher hydrophobicity exhibited lower cmc than the morpholinium-based SAIL. Furthermore, it is manifested from cmc data that the cmc of the amide-functionalized SAILs is threefold–fourfold lower than the nonfunctionalized SAILs with the same alkyl chain, whereas

![Figure 1. Chemical structures of ionic liquids (A) C16AMeImBr, (B) C16AMorphBr, and (C) C16APyBr and (D) stimuli-responsive structural transition.](Image)

| solvent | C16AMeImBr (mM) | C16AMorphBr (mM) | C16APyBr (mM) |
|---------|-----------------|------------------|---------------|
| water   | 0.18            | 0.20             | 0.18          |
| DMSO/water | 0.35           | 0.29             | 0.24          |

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somewhat lower than the ester-functionalized SAILs with the same alkyl chain length.\textsuperscript{38–43} The micellar properties of the studied AFSAILs in DMSO/water systems have not been studied previously and hence not compared. DMSO is a polar aprotic solvent, completely miscible in water and has a dielectric constant less than that of water ($\varepsilon_{\text{DMSO}} = 46.7$; $\varepsilon_{\text{water}} = 80.4$). It is having a partially negatively charged oxygen atom that forms a hydrogen bond with water and breaks the 3D structure of water to form the stoichiometric hydrates close to the ratio 1:3 (1DMSO·2H$_2$O).\textsuperscript{44} With an increased mass fraction of DMSO in water, the dielectric constant decreases; this eventually increases the electrostatic repulsion between the head groups, decreases the hydrophobic interactions, and causes an increase in cmc (Figure S2; Table 1).\textsuperscript{44} Surface-active parameters for all the three AFSAILs derived from the surface tension measurement in water and the DMSO/water system are reported in Table S1 along with the nonfunctionalized, ester-functionalized, and traditional surfactants.

Concentration- and Temperature-Responsive Reversible Structural Transition. Looking at the impact of concentration and temperature on the self-assembling behavior of surfactants in aqueous and nonaqueous media,\textsuperscript{45–49} we hereby preliminary investigated the concentration- and temperature-induced phase transformation of AFSAILs in the DMSO/water system (Figure S3A) using visual observation and turbidity measurements (at 650 nm). All the three AFSAILs show concentration-dependent phase transition from transparent solution with negligible absorbance to a bluish turbid solution (Tyndall effect) with higher absorbance to the 3D gel with the highest absorbance (Figures S3A and 2). Herein, the gel phase was analyzed by the “tube inversion test”.\textsuperscript{50–52} The wavelength of absorbance was 650 nm as neither the solvent nor the AFSAILs show any absorbance at this wavelength. Concentrations associated with the first, second, and third transitions through visual observation are reported in Figure S3.

Gel formation was observed in the ester-functionalized SAIL, 3-methyl-1-(hexadecyloxy carbonylmethyl)imidazolium bromide ($\text{C}_{16}\text{EMeImBr}$), in the equimolar composition of DMSO/water with a CGC of 8.80% (w/v).\textsuperscript{25} The lower Lewis basicity of the ester group relative to the amide group and the lower solubility of the later SAIL lead to the formation of organogels at lower concentration.\textsuperscript{25} The gelation behavior of the three studied AFSAILs in different solvents is reported in Table S2. It was found that the studied AFSAILs form a gel in DMF/water and alcohol/water systems apart from the DMSO/water system (1:3 v/v). It is inferred from the solvatochromic parameters that protic solvents, because of their ability to form a hydrogen bond with the AFSAILs, induce gelation through a delicate balance between the solvent-AFSAIL and AFSAIL–AFSAIL interactions.\textsuperscript{28,47} For the imidazolium-based amide-functionalized surfactant N-cetyl-N’-acetamidimidazolium bromide, Cheng et al. reported gelation in polar protic and aprotic solvents with a range of CGCs.\textsuperscript{48} For the ester-functionalized SAILs, the temperature-responsive ionogel was recently reported with different ranges of CGCs.\textsuperscript{15}

The organogel obtained through varying the concentration of the AFSAILs in the DMSO/water system exhibited unprecedented reversible phase behavior on increasing the temperature from RT (25 °C) to 80 °C, transforming the organogel into a free-flowing bluish turbid liquid, may be of vesicles at 40 °C, and then transparent solution, likely of smaller sized spherical micelles at 80 °C (Figures S3 and 2). The dramatic change in absorbance is associated with the change in aggregate sizes or shapes or both. The phase transition associated with the visual observation and turbidity may be due to the transformation of the spherically shaped micellar aggregates with 18–26 nm sizes to vesicles of sizes of >350 nm to organogels (lamellar shaped), as characterized by small-angle neutron scattering (SANS) measurement, \textit{vide infra}. It is to be noted here that the CGCs were 10, 12, and 14 mg/ml for $\text{C}_{16}\text{AMorphBr}$, $\text{C}_{16}\text{AMeImBr}$, and $\text{C}_{16}\text{APyBr}$, respectively (Figure S3B–D). Wang et al. reported a similar behavior for the nonfunctionalized SAILs with different alkyl chains, that is, from dodecyl to hexadecyl in an aqueous medium where the micellar aggregates are transformed into vesicles,\textsuperscript{53} whereas Du et al. observed micelles to vesicles to gel transformation in the binary solvent system.\textsuperscript{59} Temperature-induced transition data through visual observation and turbidity measurements are further confirmed through the differential scanning calorimetry (DSC) thermogram of the organogel (Figure S4). As shown in the thermogram, the gel to sol transition was observed at 39.30 °C for $\text{C}_{16}\text{AMorphBr}$, 37.89 °C for $\text{C}_{16}\text{APyBr}$, and 38.26 °C for $\text{C}_{16}\text{AMeImBr}$.

The concentration- and temperature-induced behaviors of the AFSAILs were examined through measuring the surface potential on the aggregates for the possible interactions within the amphiphiles. Stability of the colloidal system depends on the repulsive interaction between the charged micellar aggregates that inhibit their aggregation to form larger sized aggregates. This could be characterized
through measuring the charge on the colloidal particles through zeta potential (ζ), that is, if ζ is large enough (>30), the system is more stable; conversely, if ζ is small (<30), the system is more prone to agglomeration. By decreasing the surface potential, repulsion among the head groups decreases, packing at the air/solution interface increases, and critical concentration for the curvature decreases. This could result in the increased size of the aggregates and probably the shape of the aggregates too. To strengthen our hypothesis from the turbidity and visual observation, we herewith employed ζ of the studied AFSAIL systems throughout the investigated concentration regime. We observed a decrease in ζ as the concentration of all the positively charged AFSAILs increases (Figures 3 and S5). A reverse trend was observed for the ζ values once the temperature was increased from 25 to 80 °C (Figures 3 and S5), confirming the clear correlation between long fibrous 3D structures and surface potential: larger sizes have small surface potentials (vice versa). It is interesting to mention here that the value of ζ is lower in C16AMorphBr as compared to other two AFSAILs because of the strong AFSAIL–AFSAIL and AFSAIL–solvent interaction in the former (Figures 3 and S5). The morpholinium head group is lacking the aromatic π–π interaction potential and provides the lowest lipophilic interaction potential compared to other two head groups and therefore exhibits the low inhibitory potential. Free electron pairs at the oxygen atom of the morpholinium head group are weak donors or acceptors for π–π interactions. It is more likely that they are involved in strong hydrogen bonding interactions to DMSO/water molecules, making the morpholinium head group even more hydrophilic.

Compactness and polarity of the colloidal system depend on the pattern of self-assembled structures present in the system, for example, compactness of the system increases on transforming the aggregates from micelles to vesicles to gels. This could be characterized through measuring the ratio of the first and third vibronic bands I1/I3 of pyrene. The cybotactic region of pyrene experiences shift upon the formation of various morphological aggregates, the gel being the most compact with the least I1/I3 and micelles being the least compact, I1/I3 will be the highest among micelles, vesicles, and gels. With increasing concentration of the amphiphile, I1/I3 decreases, indicating that pyrene senses a more hydrophobic environment. This is attributed to the transformation of micellar aggregates from lower concentration to organogels at higher concentration with intermediate vesicular aggregates (Figure 4A). With increasing temperature, compactness of the system decreases and pyrene gets exposed to the dehydrated alkyl chains that lead to the conformational changes and a concomitant increase in the I1/I3 value, showcasing the structural transformation. It was inferred from the temperature-induced changes (Figure 4B) that pyrene senses a more polar environment, that is, I1/I3 increases with increasing the temperature of the organogel from 25 to 80 °C, suggesting the reversible phase transformation from the organogel to micellar suspension with temperature. Intermediate concentration and 40 °C, I1/I3 values at lower concentration and higher temperature indicate that the polarity of the cybotactic region of pyrene is between those of benzyl alcohol (I1/I3 = 1.22) and ethanol (I1/I3 = 1.18). At intermediate concentration and 40 °C, I1/I3 values are close to aromatic hydrocarbon solvents (i.e., benzene, I1/I3 = 0.80–1.00), whereas at high concentration and RT, that is, at 25 °C, I1/I3 values are close to aromatic hydrocarbon solvents. Among the three AFSAILs studied, I1/I3 decreases in the order C16AMorphBr > C16AMeImBr > C16APyrBr, indicating the higher polar nature of the morpholinium-based AFSAIL.

To reaffirm our results from the abovementioned techniques, SANS measurements have been employed to verify the concentration- and temperature-responsive reversible structural aggregates from a single system, the AFSAILs in the

Figure 3. Zeta potential of the C16AMeImBr system as a function of concentration and temperature.

Figure 4. I1/I3 values of the studied systems as a function of (A) concentration and (B) temperature.
DMSO/D$_2$O solvent system. SANS, an experimental technique that uses elastic neutron scattering at a small scattering angle and measures the differential scattering cross section ($d\Sigma/d\Omega$) per unit volume as a function of wave vector transfer ($Q$), gives insight into the organization of microstructures. All the samples have been prepared in DMSO/D$_2$O at a ratio of 1:3 to achieve the needed contrast between the scatterer and solvent. The SANS curves for all the systems as a function of concentration and temperatures with experimental and fitted data are shown in Figures 5, S6, and S7, Tables S3 and S4. Three distinct structural aggregates have been observed based on the varying concentrations of C$_{16}$AMeImBr at 25 °C (Figure 5A). At lower concentration (3 mg/mL), scattering is less and C$_{16}$AMeImBr has been found to form spherical micelles (characterized by the core radius). With increasing concentration to 7 mg/mL, the scattering intensity in the low-$Q$ region increases and shows a $Q^{-2}$ functionality. Modeling shows that the system consists of vesicles, and the absence of any Bragg peak in the data confirms the formation of unilamellar vesicles at this concentration. The measurement of the radius of vesicles is limited by the $Q_{\text{min}}$ of the SANS instrument, and the absence of lower cutoffs in the data indicates that the radius of the vesicle could be much larger than what can be determined from the present $Q_{\text{min}}$ that is, $2\pi/Q_{\text{min}} \sim 350$ Å. By increasing the concentration further to 12 mg/mL, the scattering pattern shows higher scattering and a distinct behavior with two correlation peaks. The ratio of peak positions (1:2) at higher $q$ is attributed to the structural transition from vesicles to lamellar structures (fibrous gel) and suggests that these lamellar structures are made up of tubes composed of polar and nonpolar layers.$^{56,59}$ On the other hand, the role of temperature in C$_{16}$AMeImBr, as depicted in Figure 5B, gives an interesting result, where the temperature-dependent SANS measurements have been carried out for a particular concentration system of C$_{16}$AMeImBr (12 mg/mL). The trend of structural transition from micelle to vesicle to lamellar for increasing concentrations (3−7−12 mg/mL) is found to follow for decreasing temperatures (80 to 40 to 25 °C) too. At 25 °C, C$_{16}$AMeImBr (12 mg/mL) forms lamellar, then forms vesicles at 40 °C, and transitions to spherical micelles at 80 °C. The SANS data for the concentration- and temperature-dependent behavior for C$_{16}$AMorphBr and C$_{16}$APyrBr are shown in Figures S6 and S7, respectively. The fitted parameters for concentration-dependent SANS data for all the AFSAILs are given in Table S3, whereas those from temperature-dependent SANS data are in Table S4. The onset of changes in SANS coincides with the onset of transitions in turbidity, phase behavior, zeta potential, and pyrene fluorescence results, *vide supra*. Furthermore, the micellar radius for all the three systems follow the order C$_{16}$APyrBr < C$_{16}$AMeImBr < C$_{16}$AMorphBr which signifies the dominant role of head group hydrophobicity.$^{60}$ Thus, SANS data support the reversible transformation from micelles to vesicles to-gels as a function of concentration and temperature. We have schematically explained the transformation in Scheme 1.

**Scheme 1. Representation of Concentration- and Temperature-Dependent Reversible Transformation**

Formation of the Organogel and Its Morphology and Mechanical Properties. Encouraged by the abovementioned results, we then extended our strategy to gelate the AFSAIL molecules at its CGC by initially dissolving them in DMSO and then gelating through the addition of the cosolvent, water. The strategy was to construct the surfactant-based organogel that can be useful for diverse applications. In a separate set of experiments, we prepared solutions of AFSAILs in respective solvents at their respective CGCs. To this, the cosolvent, water, was added so that the final composition of the mixture was 1:3. The representative gelation in the DMSO/water (1:3) system through employing the experimental condition as stated above is shown in Video I of the manuscript. The organogel thus formed exhibited identical structural characteristic that was observed through concentration-dependent organogel formation.
The organogel morphology was further examined through inverted microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). We observed that upon the addition of water into DMSO solution of ILs, the transparent solution was transformed into the fibrous network or 3D gel network (Figure 6A–I; Video 1). This is a dynamic process, taking approximately 10 min under controlled conditions of temperature (25 °C) and atmospheric pressure. The SEM images of the gel formed in the representative DMSO/water system show physically cross-linked 3D fibrous networks (Figure 7J–L), whereas AFM images (Figure 7M–O) show the formation of sponge-like fibers. As shown in AFM images of the organogels (Figure 7M–O), bundles of fibers are linked through physical interactions. A magnified view of these organogels through TEM images shows the presence of the 3D self-assembled fiber network (Figure 7P–R). SEM images of the organogels prepared in DMF, methanol, and ethanol are also presented in Figure 8.

To further elucidate the time-dependent gelation and mechanical properties of the organogel, we resorted to shear rheology experiments. In the main text of the manuscript, we have given data of representative C_{16}AMeImBr organogels. Rest two systems’ data are given in the electronic Supporting Information. Based on Winter–Chambon criteria, shear rheology at a constant strain of 0.1% was performed as the sol to gel transition took place. The tan δ for all organogels at both of the frequencies (10 and 20 rad s⁻¹) crossover at ~10 min (Figures 8A, S9A, and S10A), representing a critical point, that is, tan δc, which is the corresponding gel point from where the ratio of G″ and G′ becomes independent of the applied frequency. The scattered data after tan δc, that is, after 10 min, indicate that tan δ decreases with time and then becomes constant, representing the completion of gelation.

Furthermore, tan δ was used to estimate the (i) relaxation exponent, n, and (ii) fractal dimension d_f at the fibrous gel point from the time versus tan δ graph at two frequencies (10 and 20 rad s⁻¹) (Figures 8A, S9A and S10A). The relaxation exponent is given by tan δ = tan nπ/2, where 0 < n < 1. Based on the n values, three different regions could be assigned of n: 0.5 < n < 1, where G′′ < G′; n ∼ 0.5, where G′ ∼ G′′; and n < 0.5, where G′ > G′′. In our system, we obtain n = 0.84, 0.82, and 0.71 for C_{16}AMorphBr, C_{16}AMeImBr, and C_{16}APyBr, respectively, suggesting the highly elastic nature of the organogels at this point (Figures 8A, S9A and S10A).

Fractal dimension (d_f) was further determined from the relaxation exponent to define the 3D network structure of the organogels studied. A percolation-based theory for the fully screened excluded volume has been proposed to relate n and d_f using the correlation n = d(d + 2 - 2d_f)/(d + 2 - d_f), where d = 3 for 3D structures. Using the abovementioned relationship, d_f values of C_{16}AMorphBr, C_{16}AMeImBr, and C_{16}APyBr-based organogels have been estimated and were found to be 6.49, 6.26, and 5.56, respectively, which attributed to the hyperbranched fibers present in the organogel.

As shown in Figures 8B, S9B, and S10B, G′ and G″ crossover occurs close to the increasing time corresponding tan δc, where G′ surpasses G″ at ~10 min and then almost levels off, indicating the formation of the soft-solid-like 3D fibrous gel. The results indicate that the gel point, as determined by the Winter–Chambon criteria, is slightly different from the one defined from the G″-G′″ crossover. At this stage, G′ was about an order of magnitude higher than G″, which further confirms the formation of ionic gel or soft-solid-like materials.

The ionic supramolecular gel also displays an almost frequency-independent nature. Figures 8C, S9C, and S10C show shear modulus as a function of frequency. Results indicate that for all the organogels, G′ is higher than G″ for the studied frequency range, and they are independent of the frequency that confirms a soft-solid-like behavior. Figures 8D, S9D, and S10D display stress changes in G′ and G″ as a function of strain. Supramolecular ionic gels display a softening behavior at a low strain value, and they lose their structural integrity once they reach a large strain off, indicating the formation of the soft-solid-like 3D fibrous gel. The results indicate that the gel point, as determined by the Winter–Chambon criteria, is slightly different from the one defined from the G″-G′″ crossover. At this stage, G′ was about an order of magnitude higher than G″, which further confirms the formation of ionic gel or soft-solid-like materials.

As observed from the SANS measurements, the organogels are made up of the lamellar structures that are made up of tubes composed of polar and nonpolar layers with thicknesses of 1.5–1.9 nm. Furthermore, the thickness of the lamellar sheets is 1 order of magnitude smaller than its d spacing; thus, the fibers of these organogels can be considered relatively stiff. At higher concentration, that is, at CGC, population of the fibers is high, which eventually increases the thickness, but at
the same time, an increase in d spacing, albeit small, also occurred. These phenomena lead to higher bending modulus, which in turn leads to the higher shear modulus as observed in several molecular gels where physical cross-linking is the main
cause of gelation and the fiber diameter is much smaller than its length.\textsuperscript{69} In contrast to this, in the polymeric gels, fiber branching and local heterogeneity are not available, which leads to the concentration-dependent structural defects in the molecular gels.

To verify the cause of structural transitions and to understand the AFSAIL–AFSAIL and solvent–AFSAIL interactions during phase transitions, we recorded the FT-IR spectra of the AFSAILs in suspension and the gel form. When the FT-IR spectra of the suspension and organogel samples were prepared in solvent/water, they exhibited peaks at 1650 and 3400 cm\(^{-1}\) which are overlapped with the characteristic bands of the respective AFSAILs.\textsuperscript{70} To avoid this and get better insights into the cause of structural transition, we replace water with D\(_2\)O and prepared the gel samples in D\(_2\)O as the cosolvent. The FT-IR spectra were recorded for the solid AFSAILs and AFSAILs in the solution state (in DMSO) and in the gel state (D\(_2\)O in IL-DMSO solution) (Figure S10). Peaks associated with the \(\sim\text{N–H}\) and \(\sim\text{C=O}\) stretching frequencies within the AFSAIL get shifted to the lower frequencies (Table 2) for the AFSAIL solutions in DMSO. The shifts are more prominent in C\(_{16}\)AMorphBr as compared to the other two AFSAILs because of strong AFSAIL–solvent interactions. Once D\(_2\)O was added, the organogel was formed, and the peaks are further shifted to lower frequencies (Table 2). This band shifting to lower frequency (red shift) in gels is attributed to the presence of intermolecular hydrogen bonding between the amide \(\sim\text{N–H}\) and carbonyl \(\sim\text{C=O}\) groups with the D\(_2\)O (Figure S11; Table 2). Thus, FTIR results indicate that hydrogen bonding plays a dominant role in the phase transformation from sol to fibrous gel.\textsuperscript{71}

We further tested whether gelation is disturbed in the presence of a saturated salt solution such as NaCl and acidic or basic medium for its practical application potential.\textsuperscript{72,73} We observed that the gel remains intact up to 800 mM solution of NaCl, above which the gel was transformed into the viscous solution (Figure 9). Any structural transformation of the organogel in the highly saline medium is above the scope of this manuscript and will be communicated separately. Similarly, the organogel stability was tested in the buffer solutions. It was observed that the gel remains intact in buffer solution with 7.4, whereas at acidic (2–4) and alkaline (10–12) pH, it gets transformed into the viscous solution (Figure 9).

### Table 2. Frequency Values for Solid AFSAILs, AFSAILs in the Suspension Form, and Organogels

| functional group | ILs   | solid AFSAILs | AFSAILs in suspension | organogel |
|------------------|-------|---------------|-----------------------|-----------|
| \(\sim\text{N–H}\) | C\(_{16}\)AMelImBr | 3442 | 3373 | 3375 |
|                  | C\(_{16}\)AMorphBr | 3439 | 3425 | 3373 |
|                  | C\(_{16}\)APyBr | 3445 | 3419 | 3325 |
| \(\sim\text{C=O}\) | C\(_{16}\)AMelImBr | 1680 | 1653 | 1649 |
|                  | C\(_{16}\)AMorphBr | 1675 | 1651 | 1643 |
|                  | C\(_{16}\)APyBr | 1662 | 1660 | 1641 |

penetrating network structures. The organogels in the DMSO/water system have proven to be a very attractive method to create nanostructures that are unattainable by a single component previously. The self-assembled structures that change their shapes and sizes based on the stimuli, that is, concentration and temperature, are formed as a result of hydrogen bonding and competitive AFSAIL–AFSAIL and solvent–AFSAIL interactions. The nanostructures can mimic the complexity and functionality of natural systems such as DNA and proteins. The knowledge of structural transition within the single component was used to develop the organogels through the addition of water as the cosolvent in the isotropic solution of SAILs in the aprotic solvent, here DMSO. In principle, the self-assembly approach within the surfactant-based gelators can be extended to other molecular building blocks that can open an entirely new research field with a broad and unexplored range of nanostructures exclusively based on “weak” interactions. In future investigations, our emphasis will be on designing SAILs with tailor-made functionalization that forms nano-objects with unique characteristics. This will serve as a unique and powerful approach toward the formation of novel architectures on demand and can also act as a substitute for conventional ionic surfactants in various applications. A graphical summary of all the results is shown in Figure 10.

**CONCLUSIONS**

In conclusion, AFSAILs exhibited stimuli-responsive reversible self-assembling behavior in the DMSO/water solvent system and formed a variety of nano-objects including 3D interpenetrating network structures. The organogels in the DMSO/water system have proven to be a very attractive method to create nanostructures that are unattainable by a single component previously. The self-assembled structures that change their shapes and sizes based on the stimuli, that is, concentration and temperature, are formed as a result of hydrogen bonding and competitive AFSAIL–AFSAIL and solvent–AFSAIL interactions. The nanostructures can mimic the complexity and functionality of natural systems such as DNA and proteins. The knowledge of structural transition within the single component was used to develop the organogels through the addition of water as the cosolvent in the isotropic solution of SAILs in the aprotic solvent, here DMSO. In principle, the self-assembly approach within the surfactant-based gelators can be extended to other molecular building blocks that can open an entirely new research field with a broad and unexplored range of nanostructures exclusively based on “weak” interactions. In future investigations, our emphasis will be on designing SAILs with tailor-made functionalization that forms nano-objects with unique characteristics. This will serve as a unique and powerful approach toward the formation of novel architectures on demand and can also act as a substitute for conventional ionic surfactants in various applications. A graphical summary of all the results is shown in Figure 10.

**EXPERIMENTAL SECTION**

**Materials.** Hexadecyl amine and bromoacetyl bromide were obtained from TCI and used as received. DMSO, DMF, diethyl ether, acetone, methanol, ethanol, and ethyl acetate were obtained from Sigma-Aldrich. All solvents are of high purity (\(<\sim99\%\)).

**Synthesis of C\(_{16}\)AMElImBr, C\(_{16}\)APyrBr, and C\(_{16}\)AMorphBr.** 2-Bromo-N-hexadecylacetamides were synthesized according to the earlier procedure reported.\textsuperscript{55} 1-Aminohexadecane (25 mmol, 6.02 g) in dichloromethane (30 mL) was added dropwise to a stirred solution of bromoacetyl bromide (27.5 mmol, 5.50 g) in dichloromethane (30 mL) cooled in an ice bath. After 30 min, the ice bath was removed, and the reaction mixture was stirred for another 4 h at RT followed by neutralization with NaOH solution. The dichloromethane layer was separated using a separating funnel.

![](image.png)
and was removed from the crude reaction mixture under reduced pressure in a rotary flash evaporator at 40°C to 50°C. The crude reaction mixture was then washed with 100 mL of warm aqueous ethanol. The lower layer consisting of 2-bromo-N-hexadecylacetamides was allowed to separate in the separating funnel. It was then separated and dried using a vacuum rotary flash evaporator at 80°C for 30 min.

2-Bromo-N-hexadecylacetamides (10 mmol, 3.61 g) were then reacted with N-methyl morpholine (11 mmol, 1.11 g) or N-methyl imidazole (11 mmol, 0.90 g) or pyridine (11 mmol, 0.86 g) at 80°C for 1 h. The resulting crude mixture was cooled to 20°C. The product was washed thrice with 50 mL of diethyl ether and then recrystallized with 30 mL of ethyl acetate to get pure amide group-appended imidazolium-, pyridinium-, and morpholinum-based ILs. The structures of all of these products were confirmed by 1H NMR spectroscopy, Figure S1A–C.

C₁₆AmImBr: 83% yield; light brown solid; 1H NMR (CDCl₃): 0.8 (t, 3H), 1.19–1.27 (m, 26H), 1.6 (m, 2H), 3.4 (t, 2H), 4.4 (s, 3H), 5.6 (s, 2H), 8.1 (s, 1H), 8.6 (s, 1H), 9.1 (1H), 9.4 (s, 1H).

C₁₆AmMorphBr: 71% yield; light brown solid; 1H NMR (CDCl₃): 0.8 (t, 3H), 1.24–1.66 (s, 26H), 2.2 (m, 2H), 3.6 (m, 2H), 3.7 (s, 3H), 4.1–4.3 (m, 8H), 5.2 (s, 2H), 8.8 (s, 1H).

C₁₆APyrBr: 74% yield; light brown solid; 1H NMR (CDCl₃): 0.8 (t, 3H), 1.18–1.28 (m, 26H), 1.6 (m, 2H), 4.2 (t, 2H), 6.0 (s, 2H), 8.1 (m, 2H), 8.6 (m, 1H), 9.2 (1H), 9.6 (d, 2H).

Surface Tension Measurements. Surface tension of the AFSAIL solution was determined using a K9 tensiometer (Krüss) with a platinum–iridium ring at 25.0 ± 0.1°C. The instrument was calibrated using triple-distilled water.

DSC Measurements. The DSC measurements were performed using a METTLER TOLEDO DSC 1 STArē instrument. The DSC cell was calibrated using indium (mp 156.6°C; ΔHₙₐ₅ = 28.42 J/g) and zinc (mp 419.6°C; ΔHₙₐ₅ = 112.0 J/g). An amount of 30–40 mg of the organogel samples was introduced into the equipment (CDCl₃): 0.8 (t, 3H), 1.18

Zeta Potential Measurements. The zeta potential was determined using Horiba SZ-100 equipment with different concentrations and temperature (25, 40, and 80°C) ranges at BARC, Mumbai, India. Each measurement was repeated at least five times.

SANS Analysis. SANS measurements were performed at BARC, Mumbai, at sample temperatures of 25, 40, and 80°C. Data are presented as a function of the scattering vector, q

\[ q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \]

where λ is the incident neutron wavelength and q is the scattering angle. The effective q range obtained for a given experiment is therefore defined by the sample–detector distance and the detector size. Two sample–detector distances of 2 and 14 m were used with an incident wavelength of λ = 5 Å (Δλ/λ = 10%), providing a q-range of 0.005–0.400 Å⁻¹. The data were reduced from raw counts on the 2D detector to a radically averaged 1D scattering pattern with the assumption of radially isotropic scattering. The sensitivity of each detector pixel was calibrated by comparison of its response to a flat scatterer, and then, scattering from an empty SANS cell was subtracted. Scattering was then radially averaged (accounting for instrument configuration) to provide the intensity as a function of q. The absolute intensity scale was provided by normalizing each sample by its thickness (1 or 2 mm) and then compared to the scattering from an empty beam measurement. The data modeling program SASView was used to fit the SANS data. SASView software uses standard iterative least-square fitting in which selected parameters of the chosen model can be refined to optimize the fit. Parameters were refined from several starting points to ensure that a global (rather than a local) minimum was found. A prefactor, referred to as the “scale” factor, containing parameters such as the volume fraction and contrast, was left to float, and the value returned by the fit checked against its calculated value to confirm consistency of the fit.

Micelle.

\[ I(q) = \frac{\text{scale}}{V} \times \left(3V(\Delta \rho) \times \frac{\sin(qr) - qr \cos(qr)}{(qr)^3}\right)^2 + \text{background} \]

where scale is a volume fraction, V is the volume of the scatterer, r is the radius of the sphere, and background is the
background level. sld and sld_solute are the scattering length densities (SLDs) of the scatterer and the solvent, respectively, whose difference is Δρ.

Vesicle.

\[
I(q) = \frac{\phi}{V_{\text{shell}}} \times \left( \frac{3V_{\text{core}}(\rho_{\text{solute}} - \rho_{\text{shell}})I(q^{2}R_{\text{core}})}{qR_{\text{core}}} + \frac{3V_{\text{tot}}(\rho_{\text{shell}} - \rho_{\text{solute}})I(q^{2}R_{\text{tot}})}{qR_{\text{tot}}^2} \right) + \text{background}
\]

where φ is the volume fraction of the shell material, V_shell is the volume of the shell, V_core is the volume of the core, V_tot is the total volume, R_core is the radius of the core, R_tot is the outer radius of the shell, ρ_solute is the scattering length density of the solvent (which is the same as for the core in this case), ρ_shell is the scattering length density of the shell, background is a flat background level (e.g., due to incoherent scattering in the case of neutrons), and J1 is the spherical Bessel function J1(=\(\sin(x)/x^2\)).

Lamellar Gel. The scattering intensity I(q) is calculated as

\[
I(q) = 2\pi\Delta\rho^2T_{m}\frac{P_{\text{bulk}}(q)}{(q^2)}Z_N(q)
\]

The form factor of the bilayer is approximated as the cross section of an infinite, planar bilayer of thickness t (compare the equations for the lamellar model)

\[
P_{\text{bulk}}(q) = \left(\frac{\sin(qt/2)}{qt/2}\right)^2
\]

\[
Z_N(q) = \left(\frac{1 - \omega^2}{1 + \omega^2 - 2\omega \cos(qD)}) \right) + x_N S_N
\]

\[+ (1 - x_N) S_{N+1}\]

where

\[
S_N(q) = \left(\frac{a_N}{N}\right)[1 + \omega^2 - 2\omega \cos(qD)]^2
\]

and

\[
a_N = 4\omega^2 - 2(\omega^3 + \omega) \cos(qD) - 4\omega^{N+2} \cos(NqD)) + 2\omega^{N+3} \cos((N - 1)qD) + 2\omega^{N+1} \cos((N + 1)qD)
\]

for the layer spacing distribution \(\omega = \exp(-\sigma^2Dq^2/2)\).

Noninteger numbers of stacks are calculated as a linear combination of the lower and higher values

\[
N_1 = x_N N + (1 - x_N)(N + 1)
\]

Inverted Optical Microscopy. Time-induced gelation behavior was investigated using a Nikon Eclipse TS 100 inverted optical microscope with a high-intensity light-emitting diode eco-illumination system. After the addition of water into IL/DMSO solution, samples immediately were placed between two glass slides at RT, and the time interval gel texture was recorded with a Nikon camera.

Scanning Electron Microscopy. To investigate the surface morphology transformation by water, the 3D microstructures of all three amide-functionalized LMWGs were studied by SEM (Hitachi, S-3400N). Before SEM analysis, gel samples were mounted onto a copper disk using double-sided carbon tape and the surface was sprayed with gold coating.

Transmission Electron Microscopy. A transmission electron microscope operating at 200 KeV was used for internal gel morphology. Carbon-coated copper grids with a mesh size of 200 were placed on the freshly prepared gel for about a minute and were then removed. After carefully removing excess gel from the grid using a filter paper, samples were dried under vacuum for 1–2 h before collecting the images.

Atomic Force Microscopy. Morphological analysis was conducted using a Bruker atomic force microscope operating in the Peak Force mode with a probe. A thin layer (~1 mm) of a gel was sliced using a razor blade and was then placed on a clean microscope cover glass. The sample was then allowed to dry in a desiccator at RT for at least 1–2 h. AFM scans were performed with a scan rate of 0.5 Hz, at 512 × 512 pixels resolution, and also first-order flattened.

Rheology. Rheological measurements were carried out using a Physica MCR 301 rheometer (Anton Paar). A plate–plate geometry of 49.973 mm diameter and a default gap of 0.4 mm were used. The sol sample was transferred to the rheometer after the addition of water, and a small strain amplitude and 10 and 20 rad s−1 frequencies were applied to study the sol to gel transformation as a function of time. After the formation of the 3D structure or gelation process, frequency sweep experiment (\(\gamma_0 = 0.1\%\)) and strain sweep (frequency = 1 rad s−1) experiments were conducted. All the experiments were performed at least two times, and respective results were displayed.

Fourier Transform Infrared Spectroscopy. A Thermo Scientific Nicolet 6700 FTIR instrument was used to collect spectra at 4 cm−1 resolution by averaging over 64 scans over the range of 4000–600 cm−1. A solution consisting of the AFSAIL in DMSO/D2O (immediately after the addition of D2O) was placed on the liquid sample holder, and time-lapse spectra were collected. To avoid solvent evaporation, the chamber was covered with parafilm. The recorded spectrum was background-subtracted. The FTIR spectra were collected at 25 °C.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02397.

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Gelation in the DMSO/water (1:3) system (AVI)

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Notes

The authors declare no competing financial interest.

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