

# Novel Two-Component Gels of Cetylpyridinium Chloride and the Bola-amphiphile 6-Amino Caproic Acid: Phase Evolution and Mechanism of Gel Formation

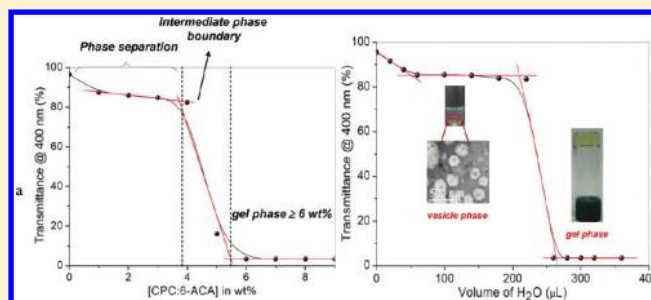
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## S Supporting Information

**ABSTRACT:** A two-component gel resulting from the amphiphilic cationic surfactant cetylpyridinium chloride (CPC) in the presence of a structure-forming bola-amphiphilic additive 6-aminocaproic acid (6-ACA) was realized and investigated. At a critical 6 wt % of 1:1 CPC:6-ACA, the yellow colored gel resulted from a 3:1 v/v CHCl<sub>3</sub>:H<sub>2</sub>O critical binary solvent composition. The mixed amphiphilic system formed a 1:1 complex with a binding constant  $\sim 0.83 \times 10^4 \text{ M}^{-1}$ . Phase evolution and mechanism of gelation in the mixed CPC:6-ACA system was unraveled upon investigating the gel microstructure, based on spectroscopic, microscopic, and small-angle X-ray scattering (SAXS) investigations. The gel assembled as a lamellar organization, maintaining a loosely interdigitated bilayer structure of CPC and 6-ACA molecules through predominant charge transfer, H-bonding, and hydrophobic and intercomplex interactions. The SAXS pattern indicated a semicrystalline form to be the stable phase with alternating crystalline and amorphous layers; a novel mode of gelation with a widely disparate semicrystalline form of the lamellar gel was thus indicated, where the lamellar structure was deduced from the interplanar spacings. A transition from low viscosity reverse micellar solution to a yellow rigid gel upon aging was thus comprehended. The mixed amphiphile in varying polarity organic solvents in the presence of water indicated the nonconductive nature of gelation in very highly polar solvents, methanol, and DMF or, in very low polarity solvents, such as, cyclohexane and carbon tetrachloride.



Surfactant molecules in solution self-assemble into structured aggregates depending on the molecular structure of the surfactant, nature of solvent and additives, and their molar composition. Ionic surfactants form spherical micelles at concentrations exceeding the critical micelle concentration; in the presence of ionic or cosurfactant additives, the reduced repulsion between the micellar head groups brings out structural transitions. Under appropriate conditions, anisotropic phase transitions of the micellar aggregates result in varied geometry of the aggregates.<sup>1</sup> With the dramatic growth of industrial and technological exploitation of surfactants, their practical applications require suitable confection of their several mixtures. The need for formulation of mixtures of surfactants arises, as real systems require optimized properties of them to meet commercial applications.<sup>2</sup> The predominant force in a colloidal system is typically electrostatic and a non-ideal mixing of oppositely charged surfactants therefore forms spontaneous microstructures of micelles, lamellar phases, vesicles, and gels.<sup>3</sup> Bola-amphiphiles are promising nonconventional surfactants exploited in mixed surfactant formulations.<sup>4</sup> The two polar head groups on either end of a hydrophobic saturated alkyl chain enable them to be efficient non-covalent solubilizers in aqueous solution, promoted by hydrogen bonding and electrostatic interactions. Bola-amphiphile-class surfactants have

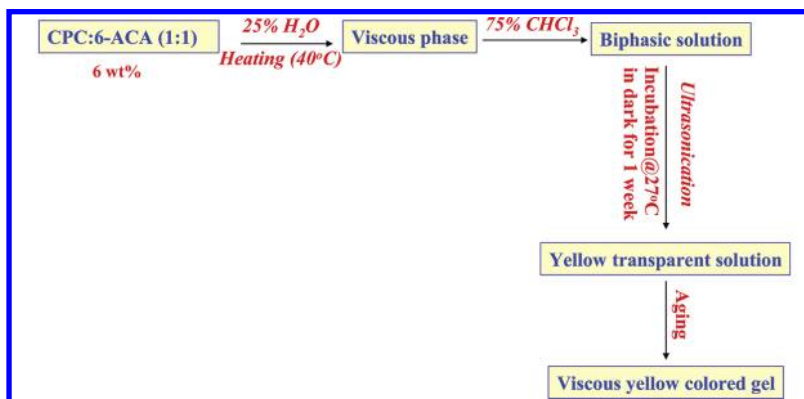
demonstrated promise to stabilize solubilized membrane proteins.<sup>5</sup> Spontaneous formation of organogels through non-covalent interactions from anionic surfactant, bis(2-ethylhexyl) sulfosuccinate (AOT) dissolved in nonpolar solvents has been reported when *p*-chlorophenol or 2,6-dihydroxynaphthalene was mixed to a 1:1 molar ratio of AOT:phenol.<sup>6–9</sup> Baddeley et al.<sup>10</sup> recently emphasized the delicate balance between both the molecular structure and electronic properties of LMWGs as well as the solvent polarity in the medium to achieve gelation and to control the morphology of the assembled fibers. It was shown that ultrasonication of supersaturated solutions is necessary to complete the sol–gel transition with gelators. The organogels formed by networks of cholesterol linkages with anthracene derivatives were studied by Weiss and co-workers.<sup>11,12</sup> Cholesterol-stilbene and cholesterol-squaraine based gels were reported by Whitten and co-workers.<sup>13–15</sup> The gel-like system formed by rod-shaped reverse micelles reported by Neuman and co-workers<sup>16</sup> and Schelly and co-workers<sup>17</sup> also formed a relevant class of materials. The chemistry and physics of

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Scheme 1. Methodology of the Two-Component CPC:6-ACA Gel Formation in 75:25 v/v CHCl<sub>3</sub>:H<sub>2</sub>O Solvent Composition

molecular gels have shown potential applications in the design and construction of smart materials.<sup>18</sup> A physical hydrogel with pH-dependence and reversibly modulated viscoelastic properties has been reported by Shi et al.<sup>19</sup>

Mixed amphiphilic systems have been proven to possess enhanced stability and spontaneous self-assembling ability when compared to most single surfactant systems, which make them explored further for newer systems. Organogelators based on organic ammonium/pyridinium salts have been recognized as structurally simple supramolecular synthons, which could permit the fine-tuning of the noncovalent molecular aggregation mode by the incorporation of selective functional groups. In comparison to conventional single component gelators, the two/multicomponent ammonium-based systems<sup>20</sup> provided additional interest allowing a further complexity of the hierarchical self-assembling process in forming higher order aggregates responsible for microphase separation in the gel state. It was reported that two component gels can assist to introduce the functional groups and obtain organogelators with functionalities in a facile way in which they interact with each other to obtain a complex by electrostatic<sup>21,22</sup> and hydrogen bonding,<sup>23</sup> and then further self-assemble via inter-complex interactions, e.g. hydrogen bonding,  $\pi$ - $\pi$ , or van der Waal's interactions to form the gel network. Confinement effects on the self-assembly of 1,3:2,4-di-*p*-methylbenzylidene sorbitol based organogel were recently reported by Chen et al.<sup>24</sup> Sulfonic acid doped thermoreversible polyaniline gels with their morphological and thermodynamical properties were studied by Jana et al.<sup>25</sup> Various multiple component gelators have also been reported in literature through donor-acceptor interaction,<sup>26–29</sup> metal ion coordination,<sup>30</sup> and acid-base interactions,<sup>31</sup> which offer the potential for developing soft materials with highly tunable microscopic and macroscopic properties. In the field of multiple components, the use of host-guest interaction was explored to create new gelling agents;<sup>20,21,32</sup> the host molecule having 2,6-(dimethylamino)pyridine moiety linked to two cholesterol groups via hydrogen bonding to a complementary barbitol guest in 1:1 ratio was reported. In the absence of the guest, the host was soluble, however, upon complexation with the guest, the formed hydrogen bonds aligned the cholesterol moieties in the host and a gel fiber was formed via van der Waals interactions.<sup>33</sup> Multicomponent systems including mixtures of gelators with complementary nongelators are known in literature, which include charge transfer interactions in the gel fiber with 1:1 molar ratio of acceptor (2,4,7-trinitrofluorenone (TNF)) to a bile acid gelator, bearing a pyrene moiety as donor molecule.<sup>29</sup> Their diverse functionality enabled them to be used in direct trapping of guest molecules without a need to capture through specific interactions. Bhattacharya et al.<sup>34</sup>

combined a weak gel with gold nanoparticles to modulate the viscoelastic properties.

Cationic surfactant cetylpyridinium chloride (CPC) is well-known for its antiseptic and antibacterial properties, while 6-aminocaproic acid (6-ACA) is a potent antifibrinolytic agent<sup>35</sup> and a bola-amphiphile. The present investigation is a first report of synthesis and structure elucidation of highly stable molecular gels from a two component mixture of cetylpyridinium chloride (CPC) and 6-aminocaproic acid (6-ACA), encouraged by ion-dipole interactions. Contributions of various intermolecular interactions and the gelator concentration, as well as the influence of solvent composition on the gelation of CPC:6-ACA has been accounted for. The mixed system is technically important in tailoring microdomain properties through simple composition variations; novel structures could be obtained by changing the system's composition, rather than through synthesis of new materials. The multicomponent surfactant systems formed thermodynamically more stable gel microstructures than single component surfactants in view of the predominant charge transfer and hydrophobic interactions along with substantial  $\pi$ -stacking.

## EXPERIMENTAL SECTION

**Materials and Methods.** Cetylpyridinium chloride of 99% purity was purchased from SD fine-chemicals Ltd., India. Conductivity measurements were done with a digital conductivity meter (Control Dynamics APX 185) with a cell constant 1 cm<sup>-1</sup>. The conductometric titrations were conducted in a jacketed cell with temperatures strictly maintained using a thermostat; ultrapure water from a Millipore Elix A3-Milli-Q system (Milli-Q, Germany) was used in preparing the aqueous solutions. Samples were prepared in freshly prepared aqueous solutions at 25 ± 0.1 °C. Electronic absorption spectra were recorded on a Cary SE double-beam spectrophotometer using a 1 cm path length Infrasil quartz cuvette. In Scheme 1, the methodology for gel formation is depicted.

**Small Angle X-ray Scattering (SAXS).** SAXS measurements were carried out using a Bruker-AXS NanoSTAR instrument with Cu K $\alpha$  radiation, operated at 45 kV/35 mA and a 2D gas detector (HI-STAR). SAXS data were recorded in the "*q*" range of 0–0.75 Å<sup>-1</sup> for 2 $\theta$  ranging between 0 and 15°.

**Transmission Electron Microscopy (TEM).** TEM images were recorded using a Philips CM12 electron microscope with a field emission electron gun at 120 keV with a resolution of 5 Å. Negatively stained images of vesicles were obtained by staining the sample with 2% phosphotungstic acid solution followed by natural evaporation at room temperature.

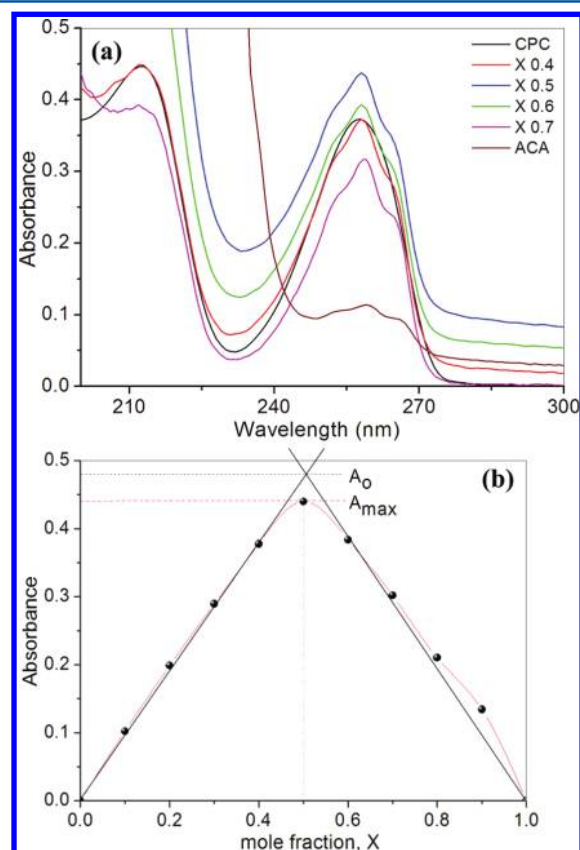
**High Resolution Scanning Electron Microscopy (HRSEM).** HRSEM images were obtained from a FEI Quanta Scanning electron microscope by placing a small drop of the sample on pretreated Si (100) substrates, followed by natural drying at room temperature in field emission mode, under low vacuum.

**Dynamic Light Scattering (DLS).** DLS experiments were carried out with Brookhaven 90 Plus particle size analyzer (Brookhaven Instruments, USA), equipped with a solid state laser operating at 15 mW power and 660 nm wavelength. The output signals were fed into a 200 channel digital correlator, which facilitated in computing the intensity–intensity autocorrelation of the scattered light. The system allowed DLS measurements at a scattering angle of 90°. Measurements were done in a special dust-free light scattering cell. About 3 mL of the sample solution was transferred into the cell for the experiment, and the temperature of the solution was maintained at 25 °C.

**Rheological Characterization.** Rheological characterization was performed using an Anton Paar 100 rheometer with a cone and plate geometry (CP 25-2\* with 2° cone angle). Time sweep measurements were performed at 25 °C with an oscillation frequency of 1 Hz at a stress amplitude of 50 Pa.

## RESULTS AND DISCUSSION

**Binding Characteristics of the Ion Associate CPC:6-ACA and Methodology of Gel Formation.** The UV–visible absorption spectral characteristic of CPC:6-ACA at varied mole fractions is shown in Figure 1a. The binding characteristics/



**Figure 1.** (a) UV–visible absorption spectra of 1:1 CPC:6-ACA solution. (b) Job's curve for the complex absorbance at 258 nm against the mole ratio showing 1:1 stoichiometry between CPC and 6-ACA.

ion-association behavior of the mixed amphiphile was investigated by adopting continuous variation method, as depicted in Figure 1b.

For a total fixed volume of 4 mL, the mole fraction “X” of 6-ACA as  $X = [6\text{-ACA}] / \{[6\text{-ACA}] + [\text{CPC}]\}$  was varied with continuous monitoring of absorbance at 258 nm. The data revealed formation of a 1:1 stoichiometric complex between CPC and 6-ACA with a binding constant  $K_b = 0.83 \times 10^4 \text{ M}^{-1}$ , (vide eqs 1 and 2) implying the electrostatic nature of the complex. For a strong electrostatic complex from cetylpyridinium chloride and picric acid,  $K_b$  was reported to be  $1 \times 10^6 \text{ M}^{-1}$ .<sup>36</sup>



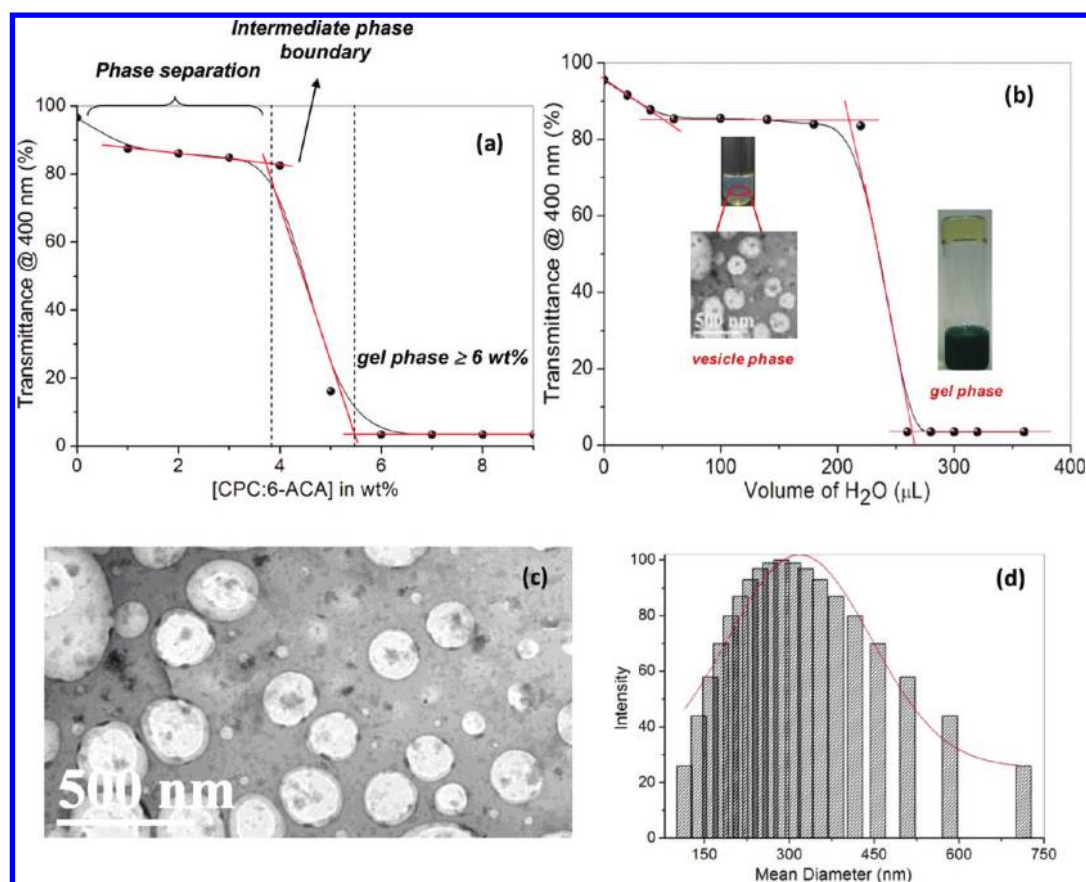
$$K_b = \frac{[\text{CPC-6ACA}]}{[\text{CPC}][6\text{ACA}]} \quad (2)$$

Figure 2a shows the critical gel concentration for 1:1 a CPC:6-ACA complex from transmittance measurements to be ~6 wt % in  $\text{CHCl}_3\text{:H}_2\text{O}$  binary solvent. The amount of water necessary for gel formation was deduced subsequently from similar transmittance experiments with varying water content, as depicted in Figure 2b. For these experiments, a mixture of CPC and 6-ACA with 1:1 mol ratio was prepared in  $\text{CHCl}_3$  upon heating at 40 °C. Ultrapure water (a few microliters) in each experiment was added to the above mixture followed by ultrasonication and slow cooling. The sample vials were tightly sealed preventing  $\text{CHCl}_3$  evaporation. After incubation at 27 °C in the dark for 1 week, the mixture formed a clear and nonviscous solution, which changed to a viscous yellow colored stable gel upon aging. The formed mixed gel was optically clear and supported its weight in the inverted vial. At concentrations <6 wt % 1:1 CPC:6-ACA, spherical unilamellar vesicles preceded the gel phase. The TEM image in Figure 2c revealed formation of unilamellar vesicles of ~300 nm, bringing spontaneous curvature to the assembly. Turbidity measurements with chloroform solution of CPC:6-ACA (vide Figure 2b) showed a sudden drop of transmittance with addition of water indicating formation of the gel phase. The gels were highly stable with the 1:1 molar ratio of CPC:6-ACA. For  $[6\text{-ACA}] \gg [\text{CPC}]$ , crystallization was favored over gel formation, and at  $[\text{CPC}] > [6\text{-ACA}]$ , a fibrous phase was observed. Hydration induced transitions to phases with higher curvature are driven by enthalpy, whereas, phases with lower curvature are driven by entropy. The gelation ability of CPC:6-ACA for various organic solvents in the presence of water was investigated using the “stable-to-inversion of a vial” method. The xerogels exhibited strong birefringence under the polarizing microscope.

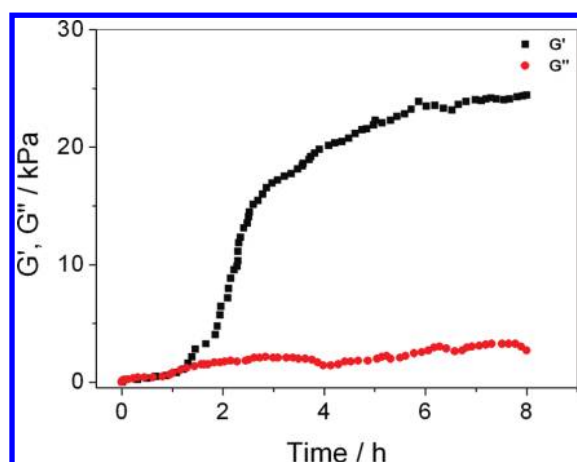
The viscoelastic properties of the gels composed of CPC and 6-ACA in binary solvent mixtures were studied through rheology experiments. The molecular gels being viscoelastic can store and dissipate energy characterized by storage modulus  $G'$  and loss modulus  $G''$ , respectively. Figure 3 shows the results obtained for 1:1 CPC:6-ACA in the binary solvent  $\text{CHCl}_3\text{:H}_2\text{O}$  (3:1 v/v). The initial values of  $G'$  and  $G''$  imply the system to behave as a viscous liquid. Upon increasing the gelation time (time > 1 h), a rapidly increasing  $G'$ , much larger than  $G''$ , indicates the formation of a network structure. After several hours at the plateau region, both components of the modulus become constant or increase very slowly with time.

The HRSEM and TEM images of the CPC:6-ACA gel shown in Figure 4a and b revealed long, entangled fibrous aggregates of 50–100 nm width and several micrometers length that stabilized the gel. The gel remained stable without any change in its appearance for at least 6 months at ambient temperature. In Table 1, the effect of solvent polarity on the gel formation is narrated. In very highly polar solvents of methanol and DMF or in very low





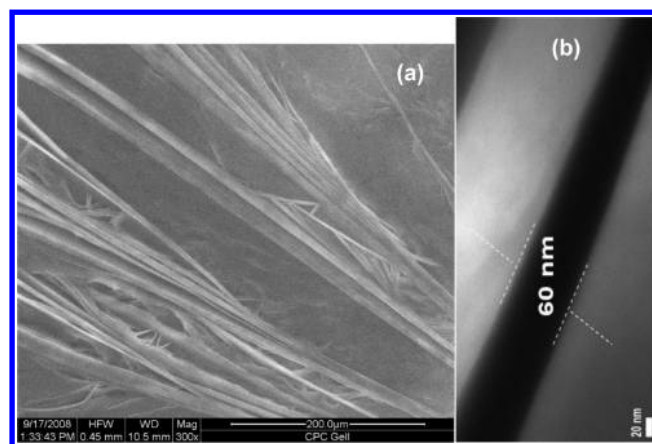
**Figure 2.** (a) Transmittance measurements as a function of [CPC:6-ACA] showing gel formation at a critical concentration  $\geq 6$  wt %. (b) Transmittance measurements showing vesicle and gel phases necessitating the required volume of water for gel formation. Insets show the stable-to-inversion of the formed CPC:6-ACA gel and the vesicular phase in the  $\text{CHCl}_3$ : $\text{H}_2\text{O}$  solvent mixture. (c) TEM image of unilamellar vesicles of size 250–300 nm. (d) DLS size distribution profile of CPC:6-ACA vesicles with a most probable size  $\sim 300$  nm.



**Figure 3.** Variation of  $G'$  and  $G''$  with gelation time for 1:1 CPC:6-ACA in the binary solvent mixture  $\text{CHCl}_3$ : $\text{H}_2\text{O}$  (3:1 v/v). The stress amplitude  $\sigma_0$  was 50 Pa.

polarity solvents, such as, cyclohexane and carbon tetrachloride, gelation was not conducive.

The cationic surfactant cetylpyridinium chloride (CPC) predominantly formed reverse micelles in chloroform but direct spherical micelles in the presence of water at a critical micellar concentration of 0.95 mM. Vesicle and gel phases were observed in binary solvent mixtures with a heteroditopic bola-amphiphile, such as the 6-aminocaproic acid (6-ACA), when it



**Figure 4.** (a) High resolution SEM and (b) TEM images of CPC:6-ACA gels showing fibrous tubular structures with uniform  $\sim 60$  nm width.

was added to the reverse micellar solution of CPC in 1:1 stoichiometric ratio over a specified range of composition. The carboxyl terminated amines were the choice in relevance to amino acids, the building blocks of biological systems. The morphology of the self-assembly was governed by the stoichiometry between CPC and the bola-amphiphile. The addition of aqueous 6-ACA solution to CPC reverse micellar solution followed by sonication induced a transition from low viscosity reverse micellar solution to a yellow color rigid gel

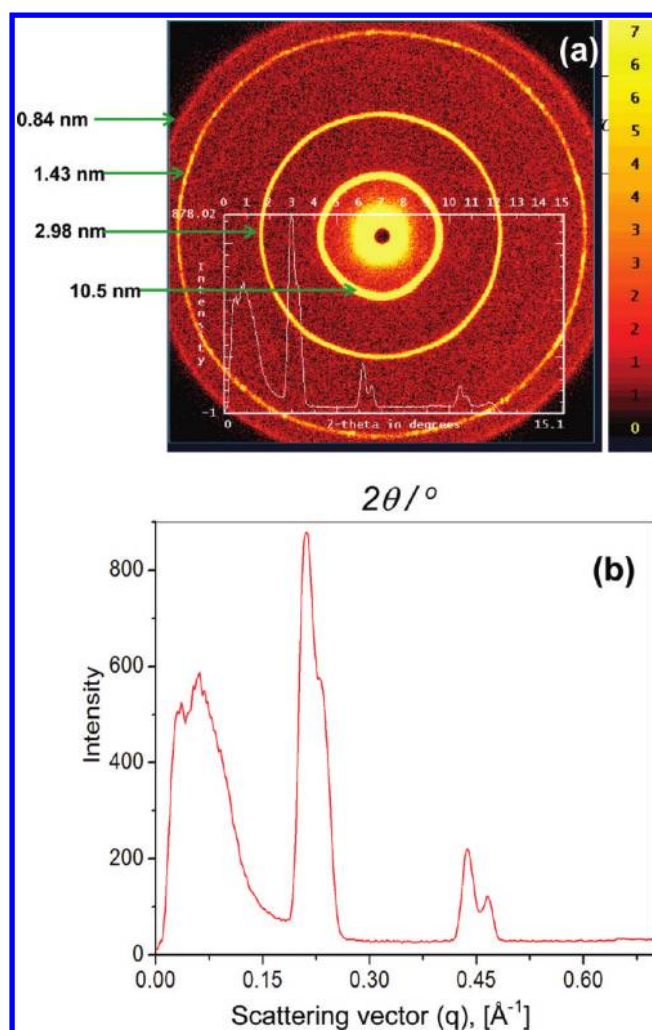
**Table 1. Effect of Solvent Polarity on Gelation of 1:1 CPC:6-ACA in the Presence of Water (25% v/v)**

dielectric constant of the solvent	appearance
cyclohexane ( $\epsilon = 2.02$ )	phase separation
carbon tetrachloride ( $\epsilon = 2.24$ )	phase separation
toluene ( $\epsilon = 2.38$ )	turbid/opaque gel (weakly viscous)
chloroform ( $\epsilon = 4.81$ )	turbid/opaque gel
dichloromethane ( $\epsilon = 9.08$ )	transparent gel
methanol ( $\epsilon = 32.6$ )	clear solution
dimethylformamide ( $\epsilon = 36.7$ )	clear solution
acetonitrile ( $\epsilon = 37.5$ )	clear solution

upon aging. Induction of phase transition from low viscosity liquids to elastic and rigid organogels<sup>37</sup> has been reported upon addition of bile salt and sodium deoxycholate to AOT reverse micellar solutions.

**Molecular Organization and Packing in the CPC:6-ACA Gel: A Small Angle X-ray Scattering (SAXS) Investigation.** The microstructure of the CPC:6-ACA gel in  $\text{CHCl}_3:\text{H}_2\text{O}$  (3:1 v/v) was investigated using small-angle X-ray scattering. The spacing between the subsequent SAXS peaks were used to distinguish the lamellar (1, 1/2, 1/3) packing from a hexagonal (1,  $1/\sqrt{2}$ ,  $1/\sqrt{3}$ ) packing. The periodic diffraction peaks and the SAXS profiles in Figure 5 reveal the calculated interplanar spacings to be in the ratio 1:1/2:1/3, indicative of the gel assembly as a lamellar organization.<sup>38</sup> Tables 2 and 3 depict the interplanar distances calculated from low angle scattering intensities and scattering vectors, respectively. A similar investigation was reported by Weiss and co-workers for organogels from primary alkyl amines as latent gelators with neutral triatomic molecules.<sup>39</sup> Molecular packing in the gel network was established in the subsequent section by comparing the “ $d$ ” values with molecular lengths.

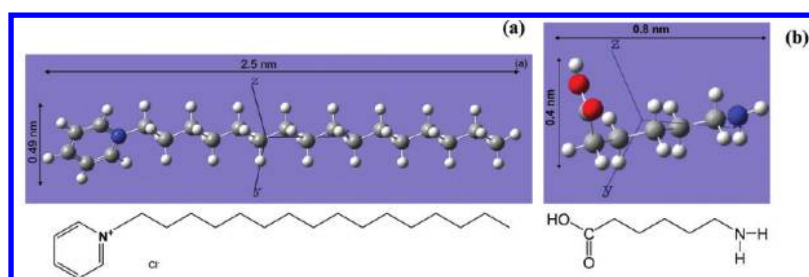
**Molecular Modeling using MM+ Force Field.** The energy minimized structures of CPC and 6-ACA are shown in Figure 6a and b. On the basis of SAXS experiments, three possible molecular packing arrangements forming a bilayer structure with periods 2.98 and 3.3 nm are conceivable; the head-to-head, tail-to-tail, and the loosely interdigitated models, as shown in Figure 7. In the first model in Figure 7a, the hydrophilic pyridinium head groups of CPC are exposed to the solvent. The second one is a molecular packing in which hydrophilic pyridinium head groups and the hydrophobic long alkyl chains occupy the outer and inner parts of the bilayer membrane, respectively (cf Figure 7b). In the third arrangement in Figure 7c, the hydrophilic pyridinium head groups and the hydrophobic long alkyl chains occupy the inner and outer parts of the bilayer membrane, respectively. The bilayer structures thus constructed were optimized using MM+ force field with geometry optimized structures of the individual CPC and 6-ACA molecules, as shown in Figure 7. For molecular modeling, the distance between alkyl chains was kept at 0.5 nm for an all-trans configuration.<sup>40</sup> The molecular arrangement for a minimum total energy of 136 kcal/mol corresponded to a loosely interdigitated packing (Figure 7c). Here, the interplanar spacing of 2.98 nm was smaller than the total extended molecular length of CPC and 6-ACA amounting to 3.3 nm but larger than the lengths of individual CPC and 6-ACA molecules. Hence, the lamellae are bilayer structures consisting of CPC and 6-ACA bilayers in which the molecules are interdigitated partially with hydrophobic interactions. On the other hand, the stabilizing interactions are predominantly

**Figure 5.** SAXS pattern (a) and spectrum (b) of CPC:6-ACA gels at 25 °C. The  $d$ -spacings calculated from  $d = \lambda/2 \sin \theta$  are marked in the figure.**Table 2. Interplanar Distances ( $d$ ) Calculated from the Scattering Vectors in SAXS of CPC:6-ACA Gels**

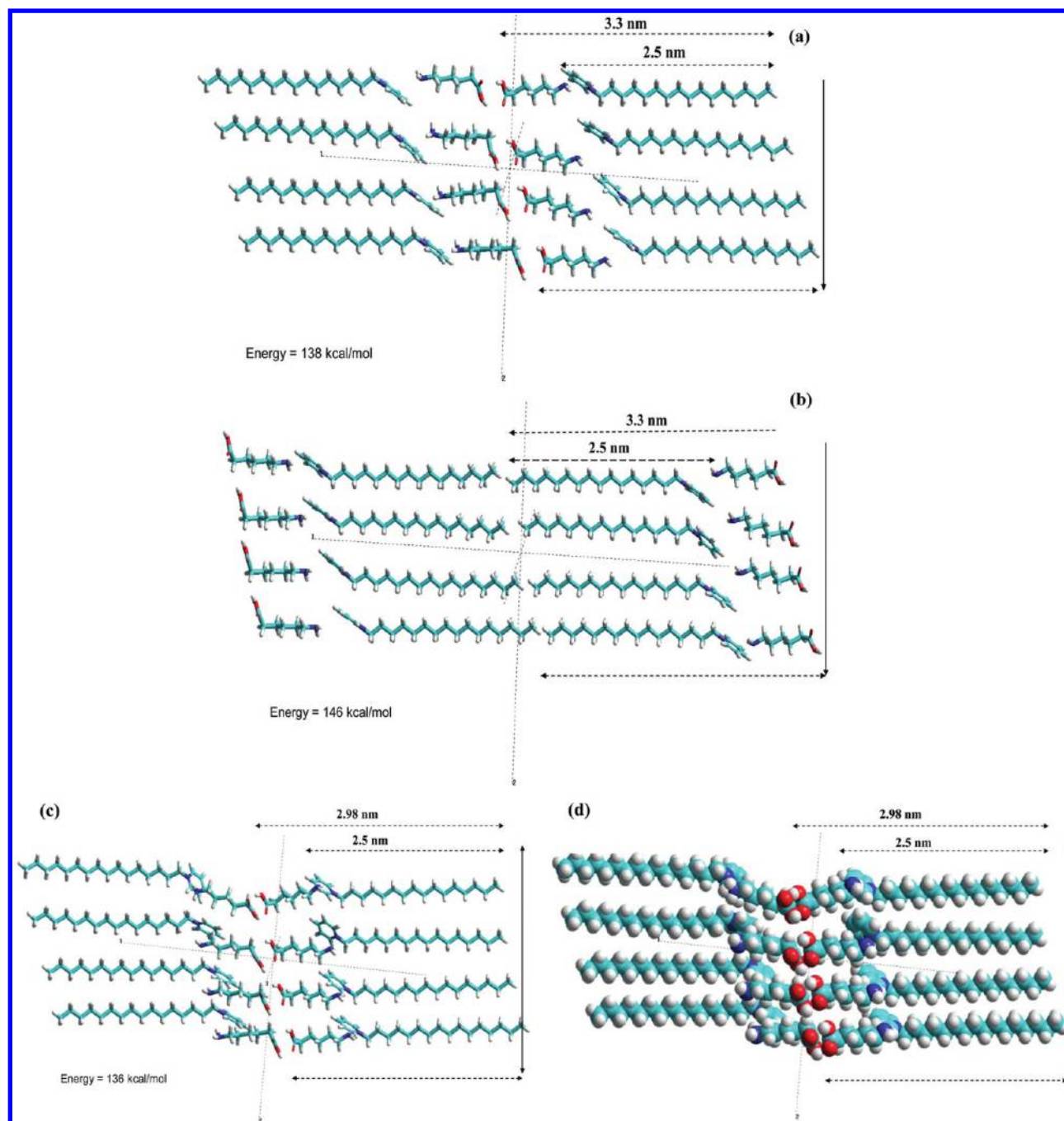
scattering vector ( $q$ ), $\text{\AA}^{-1}$	intensity ( $I$ )	interplanar distance, $d = 2\pi/q$ (nm)
0.0355	525.58	17.66
0.0612	587.94	10.26
0.2119	878.02	2.96
0.2289	576.48	2.74
0.4365	220.68	1.44
0.4649	122.07	1.35

**Table 3. Interplanar Distances ( $d$ ) Calculated from the Lowest Angle Peaks in SAXS of CPC:6-ACA Gels**

scattering angle ( $2\theta$ )	interplanar distance, $d = \lambda/(2 \sin \theta)$ (nm)
0.48	18.4
0.84	10.5
2.96	2.98
6.16	1.43
6.56	1.34
10.48	0.84
10.74	0.82
11.78	0.75



**Figure 6.** Energy minimized molecular models of (a) CPC and (b) 6-ACA using density functional calculations with B3LYP/6-31G++. Shown below are the respective chemical structures.



**Figure 7.** Molecular packing in CPC:6-ACA gel with the MM+ optimized and the energy minimized aggregate structures showing (a) head-to-head, (b) tail-to-tail, (c) a loosely interdigitated bilayer packing, and (d) CPK arrangement of the loosely interdigitated bilayer. The figures depict two pairs of CPC:6-ACA surfactant units.



of (i) charge transfer type between the pyridinium  $N^+$  and the lone pair of electrons on the  $-NH_2$  end of 6-ACA, (ii) H-bonded interactions of the carboxylic head groups, and (iii) hydrophobic interactions. In addition, the wide-angle region of the X-ray diagram for the CPC:6-ACA gels in Figure 8 revealed

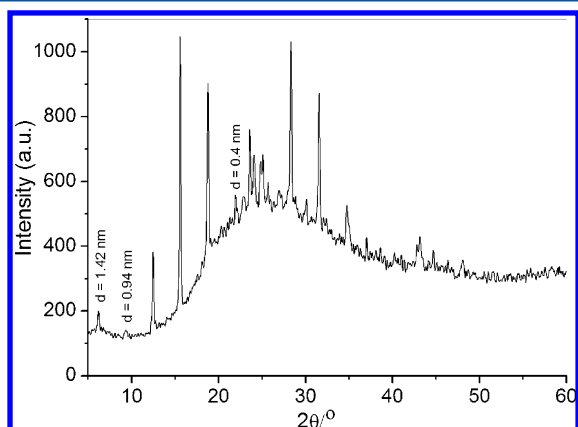


Figure 8. Wide angle XRD spectrum of CPC:6-ACA gel.

a series of sharp reflection peaks over an amorphous background, supporting the semicrystalline nature of the gel and that the long alkyl chains formed highly ordered layer packing through the extended interdigitated hydrophobic interaction, as revealed through the CPK model structure in Figure 7d. The SAXS data thus confirmed the CPC:6-ACA gels to have formed a 3-D network maintaining a loosely interdigitated bilayer structure, stabilized by charge transfer, H-bonding, and hydrophobic interactions. The results are in agreement with the aggregate structure and molecular packing in sugar-based gelators as reported by Jung et al.<sup>41</sup> The mechanism of formation of organic hydrogels from bis-urea dicarboxylic acid based molecules was reported by Estroff et al.<sup>42</sup> where powerful techniques, such as the cryo-TEM and X-ray diffraction were made use of. An extended bilayer structure is illustrated in Figure 9.

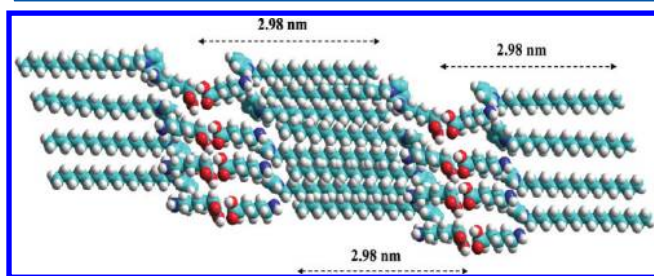


Figure 9. Extended energy minimized bilayer structure constituted with optimized CPC and 6-ACA amphiphiles.

**Mechanism of Gel Formation.** Molecular modeling of the gel fiber revealed the long polymeric association of CPC–6ACA, as shown in Figure 10. A gel could be conceived of primary, secondary, and tertiary structures akin to proteins. A primary structure is determined by recognition at the molecular level promoting anisotropic aggregation of gelators in one or two dimensions. The secondary structure of gel is influenced by the molecular structure, resulting in micelles, vesicles, ribbons, and sheets etc. The tertiary structure of the gel involves the post aggregation of structures formed from secondary

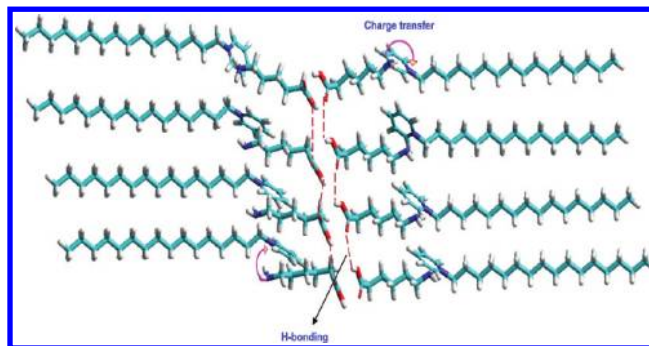


Figure 10. Schematic showing the primary ( $1^\circ$ ) and secondary ( $2^\circ$ ) structures from the 1:1 CPC:6-ACA gel; charge transfer between the amino group of 6-ACA and the quaternary  $N^+$  of the cetylpyridinium ion and, H-bonding between carbonyl ( $C=O$ ) and OH groups of carboxylic acid group are shown in a series of 2:2 CPC:6-ACA molecular model.

structures, crucial in deciding whether a molecule can form gel or precipitate from the solvent.<sup>43</sup> Charge transfer was reported recently in a dual component sugar based organogel consisting of a saccharide bearing acceptor as well as donor groups.<sup>24</sup> In the present investigation, a bilayer could result from long fibers made up of CPC and 6-ACA, which on further H-bonding with water molecules formed the secondary structures. The acquired UV–vis spectrum in Figure 11 confirms the charge transfer character of the gel at 435 nm.

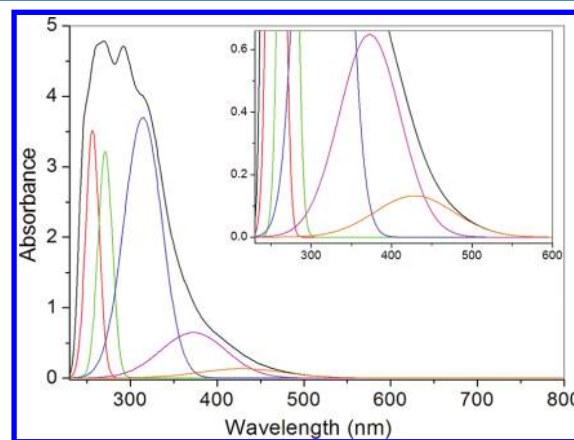


Figure 11. Experimental (black) and Gaussian fitted (colored) peaks as the UV–visible absorption spectral features of 1:1 CPC:6-ACA gel in  $CHCl_3:H_2O$  binary solvent mixture. The inset shows the expanded spectrum with the characteristic charge transfer band at 435 nm.

## CONCLUSIONS

Molecular gels from a mixed amphiphilic system of cetylpyridinium chloride and 6-aminocaproic acid at a critical solvent composition were investigated. The continuous variation method of analysis revealed a 1:1 stoichiometric complexation between CPC and 6-ACA with a binding constant of  $0.83 \times 10^4 \text{ M}^{-1}$ . The ability of CPC:6-ACA to self-assemble was examined for various solvent conditions, and the effect of surfactant concentration and solvent polarity on gel formation was studied. The variation in solvent composition induced structural transition from reverse micelles-to-vesicles-to-gels, when a chloroform solution of CPC was added to an aqueous solution of 6-ACA, followed by ultrasonication.

The reverse micelles of CPC were able to solubilize the chloroform insoluble 6-ACA with stepwise addition of water, followed by ultrasonication. The structural and dynamical parameters in the above systems were explored through molecular modeling, UV–visible transmittance and small-angle X-ray scattering, HRSEM, and TEM techniques. Molecular modeling in conjunction with SAXS studies revealed that the gels formed a 3-D network maintaining a loosely interdigitated bilayer structure of CPC and 6-ACA molecules with 2.98 nm thickness upon predominant charge transfer interaction and were stabilized by H-bonding and hydrophobic interactions. The periodical diffraction peaks from SAXS investigation indicated the gel to assemble as a lamellar organization. The formed molecular gels could provide suitable microenvironments for the regulated electrochemistry of redox active molecules, such as, fullerenes, whose multiply charged anions may lead to a variety of unique functions.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Polarized and optical microscopy images, FT-IR spectra of wet and xerogels. 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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