Intercalation in Novel Organogels with a "Stacked" Phenol Microstructure

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Abstract: In nonpolar solvents, dry reversed micelles of the twin-tailed anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) transform into a class of organogels upon the addition of suitable phenols. The gels are novel in that very small quantities of these low molecular weight solutes are sufficient to cause gelation. Hydrogen-bonding interactions between phenols and the head group of AOT form the basis for such gels. The gel–liquid transition is sharply defined and occurs over a very narrow temperature range when the gel is warmed or when trace amounts of moisture are absorbed. Evidence suggests that the underlying molecular architecture of these gels consists of strands of stacked and motionally restricted phenol molecules, with the surfactant adsorbed externally. We present further supporting evidence in this report and show that these gels can be doped with substantial quantities of a second species, leading to the formation of mixed gels. NMR evidence indicates that some of these dopants stack into the gel matrix by "intercalation" into the motionally restricted region of the aromatic strand. Factors such as the molecular shape and proton donor strength (acidity) that determine whether or not a dopant is intercalated are examined.

Introduction

Anhydrous solutions of the twin-tailed anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) are transformed into a novel class of organogels upon the addition of specific phenols in nonpolar solvents.[1] The phenomenon of gel formation is quite general and occurs in a wide variety of solvents and from a wide choice of phenols. Unlike most surfactant- or polymer-based gels, the novelty of these gels lies in the fact that they form at very small concentrations of low molecular weight precursors (AOT and the phenol). For instance, it is possible to gelate the whole solvent body with as little as 0.2% (w/v) total solute (surfactant + phenol) (i.e., 0.2 g/100 mL of solution) with proper choice of the phenol and the solvent. It was established that the underlying forces for gel formation are hydrogen-bonding associations between the phenols and the sulfosuccinate head group of the surfactant AOT.[1] Accordingly, these gels are sensitive to temperature and moisture and melt upon heating or the addition of a trace of water. Many of them are optically transparent.

Such sharply defined phase transitions are indicative of a well-defined phase microstructure. Apart from simple applications in temperature and moisture sensing, it appears that this ordered microstructure may be exploited for interesting applications in templating materials synthesis. The synthesis of highly organized structures such as ordered phenolic polymers, polymer–ceramic composites (ceramers), and semiconductor nanostructures (quantum plates, wires, or dots) seems to be possible with suitably functionalized phenols. In this paper, we examine the effects of incorporating other chemical species into these gels, to explore additional applications. Such investigations are expected to shed more light about the nature of the gels themselves.

The question of the gel microstructure was addressed in an earlier communication.[2] Many experiments of gelation were conducted with several different solvents and phenols at various concentrations. A combination of NMR and other investigations suggested that the gel structure consists of strands of ordered, motionally restricted phenol molecules. The most likely explanation is that the aromatic rings stack in the strands as indicated in Figure 1. Although this gel structure is not absolutely established by these techniques, the experimental observations including those that we present here are all consistent with this gel picture. We find that it is possible to dope the phenol aromatic stack by the intercalation of other suitable species. In this paper, we examine the nature of the chemical species that the gels admit and make some generalizations toward the properties of these dopant molecules that can intercalate within the gels.

Materials and Methods

All chemicals were analytical grade, obtained from Aldrich Chemicals, and were used as received. The surfactant AOT had a variable moisture content when purchased and was therefore dried at 70 °C for several hours which removed this moisture to a w_0 (defined as $[H_2O]/[AOT]$) below 0.4. Values of w_0 referred to in this report are with the underlying assumption that this AOT stock is completely anhydrous. Electron microscopy was conducted in a JEOL model 820 scanning electron microscope. Anhydrous, solvent-free specimens were prepared by slow evaporation of the solvent from the gel in an inert atmosphere. These specimens were subjected to microscopy either immediately or after exposure to moisture in the ambient air for several hours. Prior to microscopy, the samples were gold-coated by sputtering. The NMR experiments are described in greater detail in an earlier communication.[2] High-resolution NMR experiments were conducted on a General Electric model GE400 Omega FT-NMR spectrometer operating at 400.08 MHz for proton and 100.61 MHz for carbon (9.395 T magnet). Deuterium resonances from various solvents were used to lock the spectrometer frequency. Reference chemical shifts were those of the lock solvent expressed as equivalent proton shifts (DMSO, 2.49 ppm; $CHCl_3$, 7.7 ppm; benzene, 7.15 ppm; methanol, 3.3 ppm; acetone, 2.04 ppm), which in turn are numbers referenced to TMS at 0 ppm.

Results and Discussion

Properties of Phenolic Organogels. In our laboratory, the formation of phenol + AOT gels was observed during the course of research in enzymatic polyphenol syntheses in microemulsion

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(1) Xu, X.; Ayyagari, M.; Tata, M.; John, V. T.; McPherson, G. L. *J. Phys. Chem.* **1993**, *97*, 11350–11353.
(2) Tata, M.; John, V. T.; Waguespack, Y. Y.; McPherson, G. L. *J. Phys. Chem.* **1994**, *98*, 3809–3817.
(3) Rao, A. M.; John, V. T.; Gonzalez, R. D.; Akkara, J. A.; Kaplan, D. L. *Biotechnol. Bioeng.* **1993**, *41*, 531–540.

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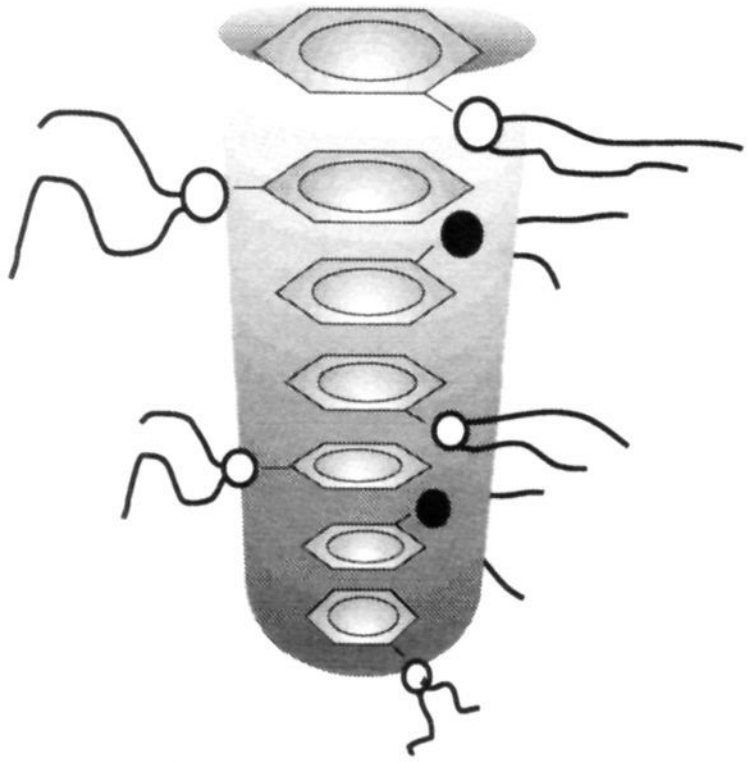

Figure 1. Schematic of the proposed gel structure. The phenol molecules are stacked to form a strand with the hydrogen-bonded AOT adsorbed on the external surface. AOT molecules are shown as twin-tailed spheres (heads). Those approaching the stack from behind are shown with black heads. It is important to note that the arrangement of AOT around the phenol stack is perhaps more random than what is shown here. The shaded region represents the hydrophilic shell that envelopes the aromatic ring stack and contains the phenol hydroxyls and the AOT head groups. The strand could be flexible and contain defects leading to cross-links.

systems.[3] The gels do not form if aliphatic alcohols are substituted for the phenols. The organogels form at an AOT/phenol ratio close to unity, and significant deviations (typically $\geq {}^{3}/_{1}$ or $\leq {}^{1}/_{3}$) lead to softening and liquefaction.[1,2] We also find that the phenol O–H stretch band of infrared absorption is significantly red-shifted upon gelation by adding AOT to phenol in solution.[1] This indicates that, in the gel state, AOT–phenol interactions dominate over phenol self-interactions. Phenols substituted with alkyl chains longer than two carbon units form gels with increasing difficulty. For instance, while 4-butylphenol forms (weak) gels in isooctane, 4-octyl- and 4-nonylphenols do not form gels. Ortho-substituted phenols, e.g. 2-cresol, 2-nitrophenol, 2,4-dinitrophenol, do not form gels. The consistency of the gel decreases with increasing deviations from an AOT/phenol ratio of 1, but a typical viscosity is about 3×10^7 cP and a typical melting point is about 30 °C (0.3 M 4-cresol/isooctane gel). Moisture absorption by an amount corresponding to as little as one H_2O molecule for every five AOT molecules causes a complete breakdown of the gel, resulting in a liquid solution with a consistency similar to that of the pure solvent.

NMR Spectra of the AOT + Phenol Gels and the Gel Microstructure. Initially, the AOT + phenol gels were characterized by infrared spectroscopy, where gelation leads to observable but relatively subtle spectral changes.[1] In contrast, gel formation was found to have dramatic effects on both the ^{1}H and ^{13}C NMR spectra. NMR spectra of a number of AOT + phenol gels were examined under a variety of conditions. In general, the resonances associated with the AOT and the solvent molecules remain well resolved in the gel phase while, at the same time, resonances associated with the phenolic species are broadened dramatically. The effect is striking as indicated in Figure 2. These data for the AOT + 4-nitrophenol gel in benzene as the solvent are typical of all AOT + phenol gels. Once the gel structure is broken down either by heating or by adding a trace of water, the phenol proton resonances appear sharp and well resolved. This broadening of aromatic proton resonances in the gels and their dramatic sharpening upon gel melting are also evident in ^{13}C spectra (not shown).

The broadening of the phenol resonances can be interpreted as an indication of severely restricted freedom of motion.[2] In the

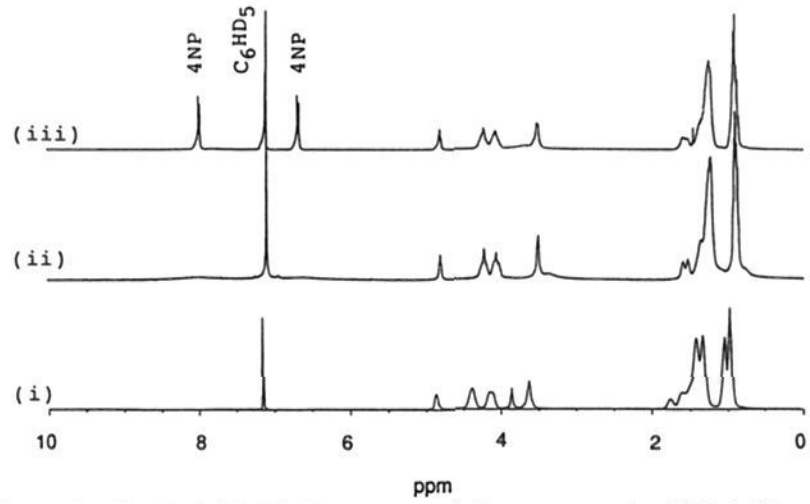

Figure 2. Typical ^{1}H NMR spectra of the organogels. 4NP indicates 4-nitrophenol resonances. The other peaks are AOT resonances and are discussed in detail in an earlier paper.[2] (i) 0.2 M solution of AOT in C_6D_6. (ii) 0.15 M each of 4-nitrophenol and AOT in C_6D_6 (a gel). (iii) The same gel as in ii, melted by exposure to moisture in ambient air ($w_0 \approx 0.4$).

gel state, the motions of phenol molecules are characterized by a long time scale relative to the NMR time scale. In such a situation, the magnetic field sensed by the phenol molecules is not orientationally averaged, giving rise to the observed spread of resonance frequencies for each of the NMR active nuclei in the phenol. In this paper, we use this observation as a signature of rigidity and as a tool to address the localization of various dopant molecules. Specifically, a significant broadening of dopant ^{1}H and ^{13}C resonances is an indication of intercalation into the rigid portion of the gel strands.

The formation of a gel indicates that the addition of a phenol to AOT in solution results in an ordered and extended structure. The formation of cylindrical aggregates by stacking is suggested by two observations. First, the gels can be formed at extremely low concentrations (e.g., 4-nitrophenol can form gels at 3 mM in isooctane). This observation indicates the presence of a network of strands throughout the solvent. Next is the NMR mobility information which indicates that phenol behaves "solid-like" whereas AOT retains fluid mobility. It follows that the most likely structure for the strands is the one made up with stacked and motionally restricted phenol molecules.[2] The surfactant is externally adsorbed and is free to assume various conformations as indicated by NMR spectroscopic evidence.

In accordance with this picture, a largely one-dimensional structure could be seen in electron micrographs of dried, solvent-free gels. Figure 3a shows a scanning electron micrograph of the solid fraction (AOT + phenol) of a 0.15 M 4-nitrophenol + 0.15 M AOT gel made in benzene. The solvent was allowed to evaporate slowly in a moisture-free, inert atmosphere. Fibrous structures can be clearly seen in the micrograph shown here. As the solvent is removed, the gel strands collapse into a close-packed arrangement that retains its gross one-dimensional nature to the limit of complete solvent removal. This dry material can be redissolved in benzene or other suitable nonpolar solvents to produce the gel state once again. When this dry residue is exposed to the moisture in the ambient air for several hours, traces of water are absorbed into the outermost layers, causing a partial breakdown of the structure. The effect can be clearly seen in Figure 3b, in complete accord with the NMR spectroscopic findings.

Phenol pK_a and Gel Strength. The hydrogen-bonding of phenols with the AOT head group has been studied earlier by Magid and co-workers[4] using vibrational fine structure analysis of the phenol UV absorption. These studies on the interaction between phenols and AOT reversed micelles revealed that the binding increases with increasing phenol acid strength. AOT also hydrogen-bonds to alcohols in addition to phenols; however, the binding constants

(4) Magid, L. J.; Kon-no, K.; Martin, C. A. *J. Phys. Chem.* **1981**, *85*, 1434–1439.

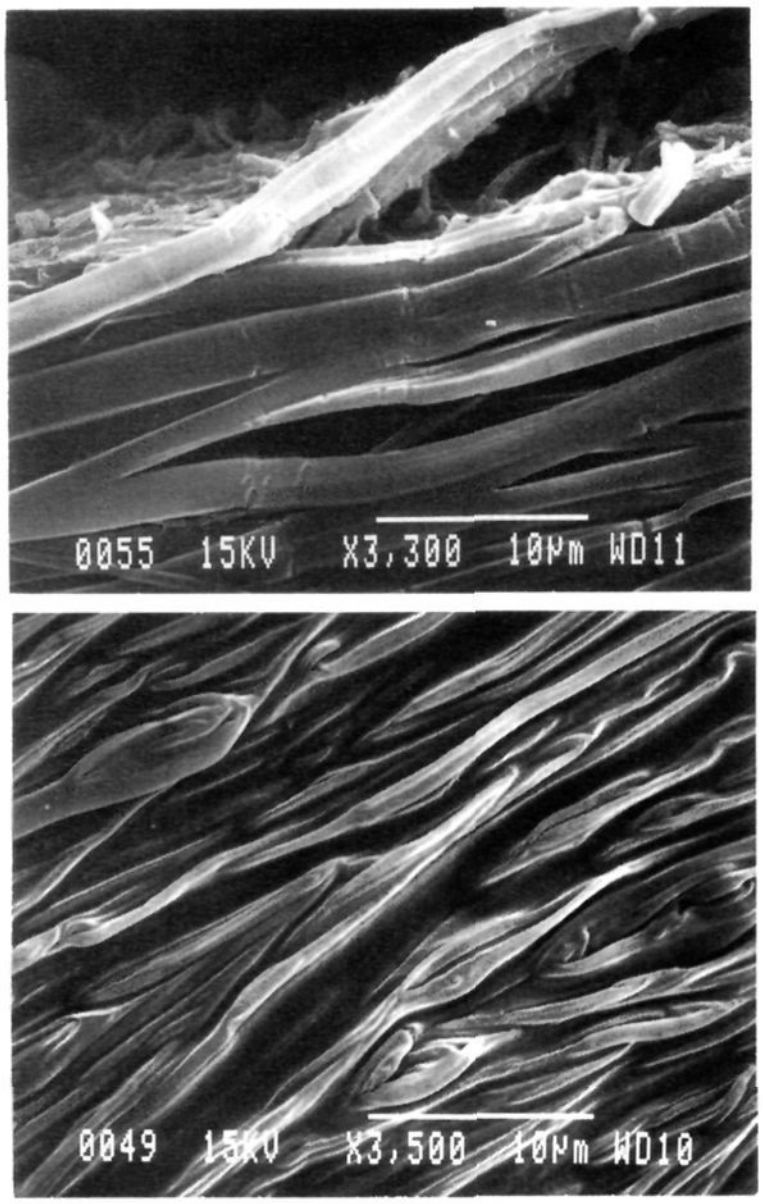

Figure 3. Scanning electron micrographs of solvent-free gels. (a) The sample was prepared by slow evaporation of the solvent from a gel of 0.15 M each of 4-nitrophenol and AOT in benzene. Subsequently, it was gold-coated and used for microscopy. (b) Same specimen as in a but exposed to moisture in ambient air for several hours prior to gold-coating.

are lower by 1–3 orders of magnitude.[5] The strength of the gel can therefore be expected to depend naturally on the acid strength of the proton donor, the phenol. Thus, while cresol (pK_a = 10.2, 25 °C in H_2O)[6] cannot form stable gels at concentrations lower than 0.1 M in isooctane, nitrophenol (pK_a = 7.15)[6] can gelate the whole solvent body at 3 mM (<0.2% (w/v)) total solute. In fact, nitrophenol forms clear and stable organogels in benzene, whereas cresol does not. Although nitrophenol is insoluble in benzene, the presence of AOT facilitates solubility, probably as the result of hydrogen-bonding. Depending on the combination of phenol and the solvent employed, the gels are clear, translucent, or opaque.

If the melting point of the gel is used as a measure of gel strength, gels made with a phenol of a higher acid strength can be expected to have a higher melting point. In Figure 4, the melting points of several gels are plotted as a function of their phenol content ([phenol]/[surfactant] = 1 in all these cases). For a given solvent, it can be seen that the melting points of 4-nitrophenol gels are consistently higher than the 4-chlorophenol or the 4-cresol gels, in accordance with the expected trend. The gel–liquid transition is relatively sharp, and the melting point can be defined to an accuracy of ±0.6 °C. It is this sharpness of the melting transition that is noteworthy and sets these gels apart from typical polymer-based gels.

A few related observations need to be discussed further here. For a given phenol, as one varies the solvent from benzene to carbon tetrachloride to isooctane, the melting points occur at higher temperatures at any given concentration as can be noticed from Figure 4. In fact, stable gels can be formed at 3 mM concentration with 4-nitrophenol in isooctane solvent at room

(5) Menassa, P.; Sandorfy, C. *Can. J. Chem.* **1985**, *63*, 3367–3370.
(6) Lide, D. R. *Handbook of Chemistry and Physics*; CRC Press: Boston, MA 1990.

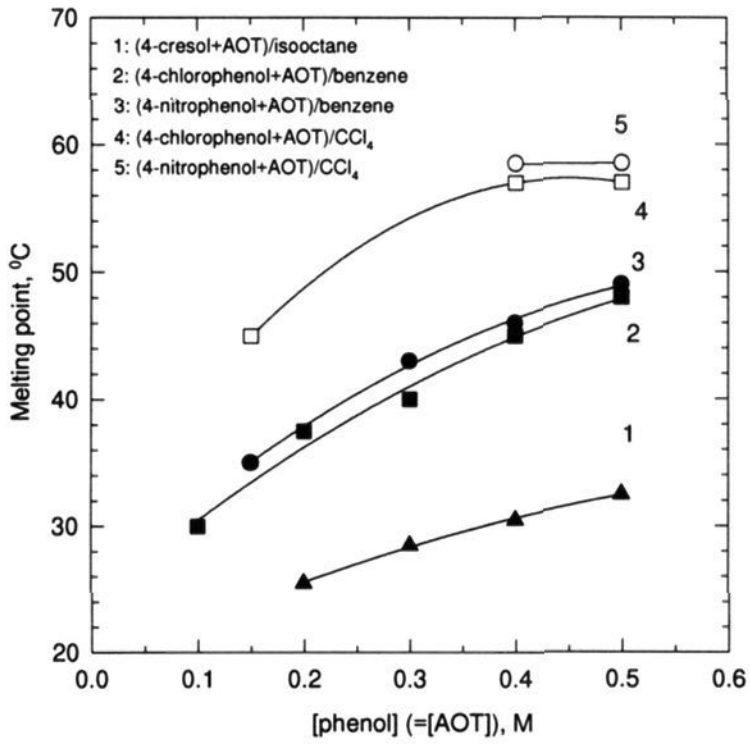

Figure 4. Melting temperatures for various gels (values reported here are accurate to ±0.6 °C).

temperature (data not shown). Further, this gel melts at ca. 60 °C despite the small concentrations of the phenol and the surfactant. The gel strength varies according to a trend when the solvent is changed. This solvent dependence may be attributed to the differential solvation of the gel strands by various solvents.[2] Magid and Martin, in their NMR study of AOT reversed micelles, argue that the degree of solvent penetration into AOT tails decreases in the order benzene > carbon tetrachloride > isooctane.[7] Thus, for a gel made in benzene, the solvent can be expected to penetrate and interact with the gel framework to a greater extent than that in carbon tetrachloride or isooctane. Finally, we observe that the melting temperatures for gels of the more acidic phenols actually approach the normal boiling points of some of the solvents.

NMR Spectroscopy of Doped Gels. Since the strength of AOT–phenol interaction is directly related to the acid strength of the phenol, it would be interesting to see if a phenol of lower acid strength could be displaced by titrating with a more acidic phenol. Another way of observing such a phenomenon is by raising the temperature of a gel containing two (or more) different phenols and look for sharpening of the less acidic phenol resonances. One such experiment was conducted with the following formulation: 4-chlorophenol (0.2 M), 4-cresol (0.1 M), and AOT (0.2 M) in a 95% (v/v) carbon tetrachloride and 5% (v/v) deuteriobenzene mixture. The deuteriobenzene here serves as a deuterium source for locking the NMR spectrometer frequency against drift. We note here that 4-cresol cannot form gels in this solvent. Interestingly, however, such a formulation results in a clear, stable gel. This is not entirely surprising because the gels do normally remain stable over a range of [phenol]/[AOT] ratios. Nevertheless, this observation demonstrates that gels can be formed when two different phenols are present simultaneously, even when one of the phenols is incapable of causing gelation in the particular solvent.

A room temperature proton NMR spectrum of this mixed gel is presented in trace i of Figure 5. The spectrum reveals a dramatic broadening of not only the chlorophenol resonances, but also the cresol resonances. This is true for the methyl protons at 2.1 ppm as well as the aromatic protons at 6.53 and 6.76 ppm. The fact that cresol resonances are severely broadened in the gel state suggests that cresol is also incorporated into the "rigid" portion of the gel structure, and does not exist as "free" phenol outside the gel matrix. Evidently, the cresol molecules in the gel phase coexist with chlorophenol in the gel stack, as an intercalated dopant.

Changes in the ^1H NMR spectrum were then followed as the gel was warmed in small temperature increments. Figure 5

(7) Martin, C. A.; Magid, L. J. *J. Phys. Chem.* **1981**, *85*, 3938–3944.

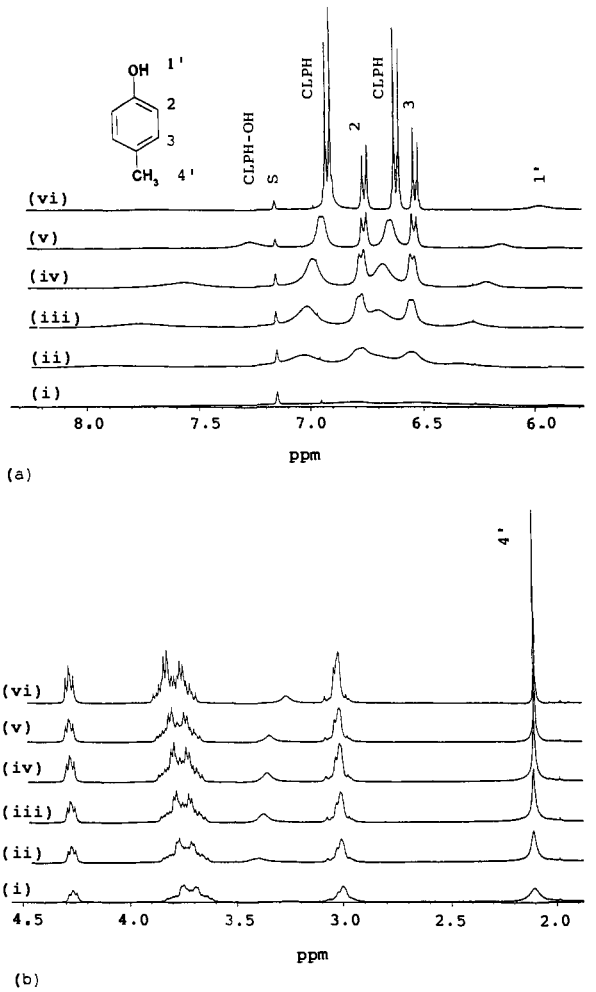

Figure 5. Gel doping with 4-cresol. Changes in ^1H spectra of a mixed gel were followed at various temperatures. The gel was made in a solvent containing 95% (v/v) CCl_4 and 5% (v/v) deuteriobenzene and contained 0.2 M 4-chlorophenol, 0.2 M AOT, and 0.1 M 4-cresol. (a) Portion of the spectrum showing the aromatic and phenol hydroxyl proton resonance region and (b) AOT and the cresol 4-methyl proton resonances: (i) 19 °C, (ii) 25 °C, (iii) 30 °C, (iv) 35 °C, (v) 40 °C, (vi) 50 °C. The resonances of the cresol protons are indicated according to the numbering scheme shown. CLPH and CLPH-OH indicate the chlorophenol aromatic ring proton and the chlorophenol hydroxyl proton resonances, respectively. S denotes the C_6HD_5 resonance from the solvent.

illustrates the temperature effects on the spectra, and we note the following observations. As the temperature rises, the resonances from both the phenols gradually sharpen so that, when the gel ultimately melts, the resonances are all well resolved. Until the gel has melted, however, the cresol resonances are always sharper than those of the chlorophenol. The sharper resonances suggest that the motion of the cresol molecule is not as restricted as that of the chlorophenol and that cresol is preferentially "extruded" from the rigid portion of the gel strands. Since only one set of cresol resonances is observed, the extrusion process must be gradual with a rapid equilibration of all the cresol environments.

Interestingly, it can be seen that the (broad) resonances of the hydroxyl protons of both phenols (Figure 5a) remain separated and distinct, indicating that these protons do not exchange on the NMR time scale in the gel state. This finding also suggests that the hydroxyl groups of neighboring phenol molecules in the gel stack probably do not interact. It is also observed that the peak at 3.2 ppm (e.g., at 50 °C), which is due to the residual moisture in AOT, remains separate from phenol hydroxyls and does not exchange with them. This water resonance is also severely broadened in the gel state, suggesting that the water molecules are confined to the thin hydrophilic shell that envelopes the aromatic stack.

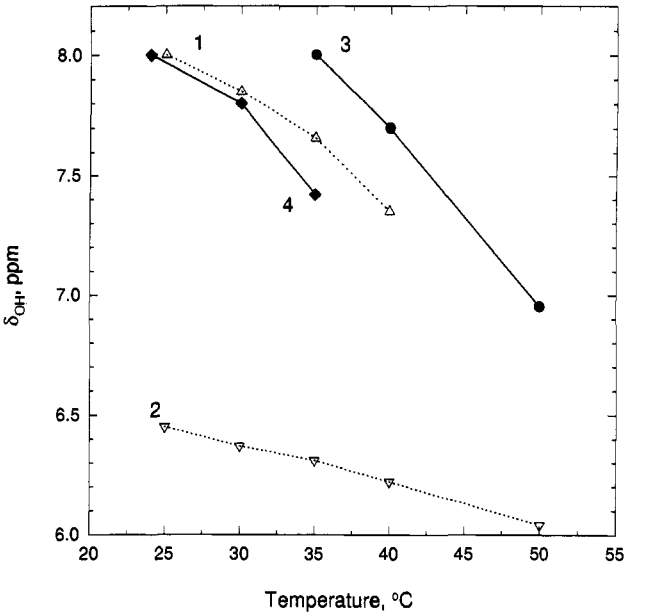

Figure 6. Temperature sensitivity of phenol hydroxyl proton chemical shifts δ_{OH}. 1: δ_{OH} for 4-chlorophenol in a doped gel containing 0.2 M each of AOT and 4-chlorophenol and 0.1 M 4-cresol in CCl_4. 2: δ_{OH} of 4-cresol in the same gel of plot 1. 3: δ_{OH} of 4-chlorophenol in an undoped gel containing 0.2 M each of 4-chlorophenol and AOT in CCl_4. 4: δ_{OH} of 4-cresol in an undoped cresol gel containing 0.4 M each of 4-cresol and AOT in isooctane.

Several other phenols (e.g., 4-nitrophenol and 2-naphthol) also form stable mixed gels such as the one discussed above. Clearly, the process of forming gels with two or more phenols being present simultaneously is quite general, provided at least one of them is capable of forming gels in the particular solvent and is present in appreciable concentrations.

Hydrogen-Bond Breakage in Doped Gels. An indication of the relative strengths of hydrogen-bonding interactions in the gels may be obtained by inspecting the temperature sensitivity of the hydroxyl proton chemical shifts (δ_{OH}) as the gel melts. At room temperature, none of these proton resonances can be accurately localized due to severe line broadening, but slight warming of the gels causes sufficient mobility of the hydroxyl protons to be discernible. Variation of δ_{OH} with temperature change is then followed, and the results are plotted in Figure 6. The progressive decrease of δ_{OH} observed in all cases as the temperature is raised is in the expected trend of diminished hydrogen-bonding interactions at higher temperatures. For the mixed gel examined in the previous section, it can be seen that 4-chlorophenol (plot 1) exhibits a larger change in δ_{OH} with changes in temperature than 4-cresol (plot 2). Thus, δ_{OH} changes very dramatically for the more acidic phenol, which is in fact largely responsible for holding the gel framework intact. The changes are less dramatic for the less acidic phenol (cresol), which in relative terms is weakly hydrogen-bonded to the AOT.

It appears that the temperature sensitivity of δ_{OH} diminishes following gel doping. For instance, for a pure (i.e., not doped) chlorophenol–AOT–CCl_4 gel (plot 3), δ_{OH} changes by a greater extent than in a cresol-doped gel (plot 1) for the same temperature change. For the doped gel, average temperature sensitivities are –0.029 and –0.017 ppm/K for 4-chlorophenol and 4-cresol, respectively. It may be noted that δ_{OH} for the 4-chlorophenol hydroxyl proton in an undoped 0.2 M gel (without cresol) is much larger, about –0.076 ppm/K (plot 3). Similar behavior is noted upon comparing the δ_{OH} data for the cresol–AOT–isooctane gel (plot 4, slope = ca. –0.05 ppm/K) to that of cresol in the cresol-doped chlorophenol gel (plot 2, slope = ca. –0.017 ppm/K). These approximate values of temperature coefficients are calculated from the slopes of the early portions of the curves such as in Figure 6. The decrease in temperature sensitivity following gel doping could be the result of a deviation from the optimum

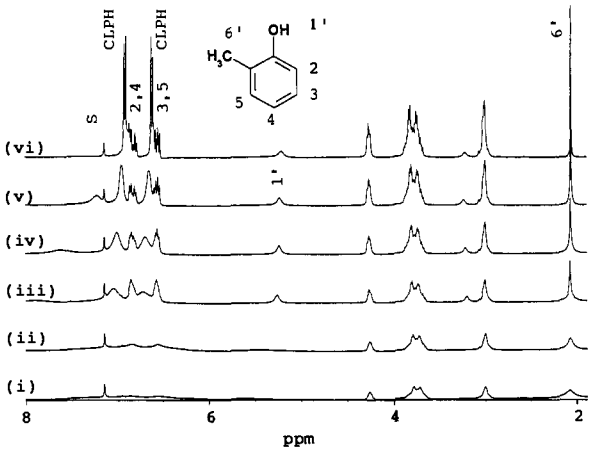

Figure 7. Gel-doping experiment with 2-cresol. This is a preparation identical to that of the gel used in Figure 5, except 2-cresol is used instead of 4-cresol: (i) 25 °C, (ii) 30 °C, (iii) 35 °C, (iv) 40 °C, (v) 45 °C, (vi) 50 °C. The cresol resonances are labeled according to the numbering scheme shown.

[AOT]/[phenol] ratio of 1, and also perhaps of the fact that the second phenol is of a smaller acid strength. To compare, water, in a $w_0 = 20$ ($w_0 = [H_2O]/[AOT]$) reversed micellar solution in isooctane, shows a much lower value of –0.0089 ppm/K. At this w_0, most of the water is "free" and the variation of chemical shift with temperature is perfectly linear, in agreement with earlier reports (not shown here).[8,9]

Steric Factors for Gel Doping. Both 4-chlorophenol and 4-cresol used in the earlier experiment are individually capable of forming gels with AOT provided a proper choice of solvent is made. Once the gel matrix is formed with a suitable (phenol + solvent) combination, another phenol is readily incorporated into this framework. With this consideration, we next examine species that retain the planar nature of the proton donor but are incapable of forming gels by themselves in *any* solvent.

We first consider 2-cresol. This phenol does not form gels although it has been shown to hydrogen-bond to AOT reversed micelles.[2,4] The reason for the loss in gel forming ability by such a subtle change in the substitution pattern for phenols has been previously described.[2] In all the gels, a close interaction between AOT and the phenol seems to be required as suggested by the common finding that the proton H-1 of the AOT molecule undergoes a downfield shift following gelation. Such downfield shifts of the resonant frequency in the vicinity of an aromatic molecule are well-known and are attributed to local anisotropies induced by ring currents.[10] Such observations have been used, for instance, to identify the partitioning locus of various species in microemulsion systems.[11] In ortho-substituted phenols, such a close interaction with the AOT head group is sterically hindered and thus gel formation by such phenols seems to be impossible.

Figure 7 shows the NMR spectra of a 0.2 M chlorophenol gel doped with 2-cresol (0.1 M). Interestingly, at room temperature, 2-cresol resonances are as severely broadened as, for example, 4-cresol resonances in single-component 4-cresol gels. Analogously, we conclude that 2-cresol also is capable of intercalating with the gel aromatic stack. At higher temperatures, this dopant is also extruded from the gel structure earlier than the main gel-forming species, 4-chlorophenol. An interesting observation with this gel is that the frequency of the 2-cresol hydroxyl proton resonance (ca. 5.3 ppm) exhibits a very weak temperature dependence, suggesting a weaker hydrogen-bonding interaction. Cresols are interesting examples to study the cases where the overall "phenol nature" of the dopant is not compromised. The first (4-cresol) differs only in acid strength from chlorophenol and therefore is incapable of forming gels by itself in this solvent. The second (2-cresol) is similar in acid strength to 4-cresol but is unable to form gels (in any solvent) due to steric hindrance from the substitution. Nevertheless, both the cresols seem to intercalate the gel stacks and coexist with the main gel-forming 4-chlorophenol. Next, we examine certain non-phenol structures for their ability to stack with the gel structure.

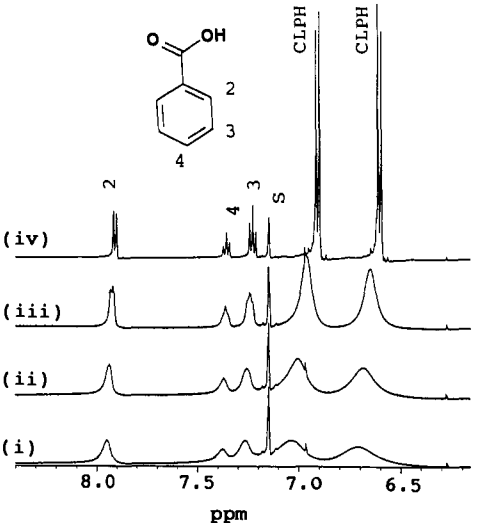

Figure 8. Gel doping with benzoic acid. Only the aromatic proton region is shown. The gel has 0.1 M 4-chlorophenol, 0.1 M AOT, and 0.02 M benzoic acid with a mixture of 95% CCl_4 and 5% benzene as the solvent: (i) 20 °C, (ii) 25 °C, (iii) 30 °C, (iv) 35 °C. The benzoic acid resonances are labeled according to the numbering scheme shown.

Acid Strength of the Dopant. If the acid strength is of prime importance, an interesting dopant candidate that is slightly different from the phenols is benzoic acid. Benzoic acid forms strong intermolecular hydrogen-bonds and exists as dimeric species in nonpolar solvents and in the vapor state. It is only sparingly soluble in isooctane, even in the presence of AOT. However, when (benzoic acid + AOT) and isooctane mixtures are heated until a clear solution is obtained and then rapidly cooled so as to cause immediate precipitation of benzoic acid, the entire solvent can be gelated. This finding indicates that AOT can perhaps break the dimers and form gel-type adducts with benzoic acid in isooctane. Such gelation does not occur in the absence of AOT, suggesting that the interactions in the gel formed are perhaps similar to those in phenolic organogels. Gel formation does not occur in this system when these solutions are cooled more gradually, indicating a kinetic control of the process; thermodynamically, hydrogen-bonding for benzoic acid dimers is probably favored. Also, such benzoic acid "gels" do not form in other solvents such as carbon tetrachloride or benzene in which benzoic acid has better solubility, indicating that perhaps factors other than acid strength are also important.

While benzoic acid cannot form the phenolic-type gels by itself, there is a possibility that it can coexist with a preformed gel framework. To see if benzoic acid can intercalate into the gel stacks, NMR spectra of a 0.1 M 4-chlorophenol gel containing doped benzoic acid (0.02 M) are then recorded. The spectra at different temperatures are shown in Figure 8. Lower concentrations are employed here in order to decrease the chances of benzoic acid self-associations (yet keeping similar relative amounts of all species). It can be seen from trace i of Figure 8 that the benzoic acid resonances are also broadened in the gel (room temperature) in a manner similar to cresol resonances in the cresol-doped gels (Figures 5 and 7, trace i).

Up to this point, only acidic molecules have been used as dopants, and all of these show an ability to stack with the gel framework. The common structural feature in all these dopants is that, apart from being acidic to varying degrees, they all possess

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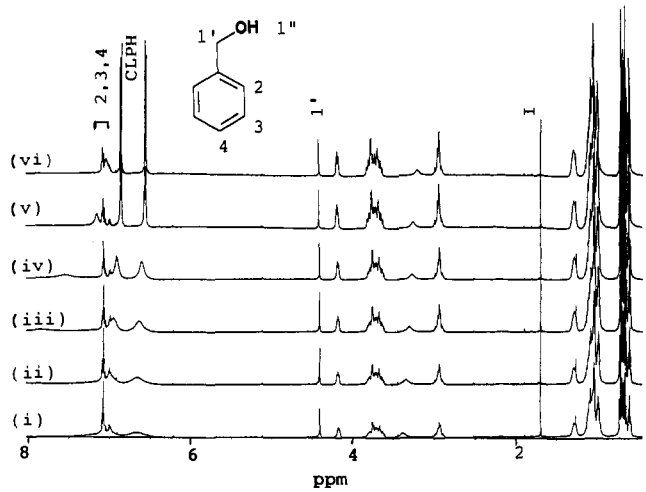

Figure 9. Gel doping with benzyl alcohol. The gel has 0.2 M each of 4-chlorophenol and AOT and 0.04 M benzyl alcohol in the 95% CCl_4 and 5% deuteriobenzene solvent: (i) 20 °C, (ii) 25 °C, (iii) 30 °C, (iv) 35 °C, (v) 40 °C, (vi) 44 °C. Resonances of the dopant are labeled according to the numbering scheme shown. The sharp peak labeled I (1.77 ppm) is due to an impurity in CCl_4.

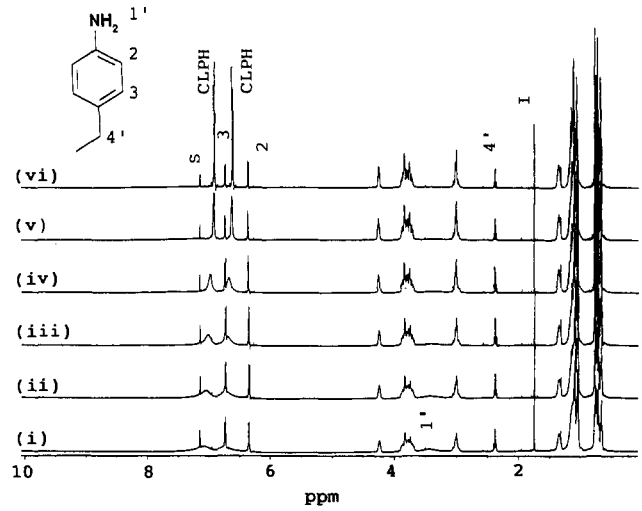

Figure 10. Gel doping with ethylaniline. The same gel used in Figure 9 was doped to 0.04 M of ethylaniline instead of benzyl alcohol: (i) 20 °C, (ii) 25 °C, (iii) 30 °C, (iv) 35 °C, (v) 40 °C, (vi) 45 °C. Resonances of the dopant are labeled according to the numbering scheme shown.

a planar aromatic ring. It is clear that such a planar geometry of the dopant facilitates sliding into the gel strands and docking to an AOT head group that is adsorbed on the rim of the aromatic strand. Understandably, the presence of this aromatic ring in the dopant is of prime importance because neither aliphatic alcohols or acids form individual or combined gels with AOT.

If we examine benzyl alcohol, which in principle, is capable of hydrogen-bonding but is not as acidic as the phenols, we find that it does not stack into the gel structure. The results of NMR experiments where a chlorophenol gel is doped with benzyl alcohol are shown in Figure 9. It can be seen that, at all temperatures, the protons of benzyl alcohol exhibit sharp and highly resolved resonances, indicating excellent freedom of motion. Perhaps another factor contributing to the inability of benzyl alcohol stacking is the intervening methylene group which cannot be accommodated if the molecule is intercalated in the gel stack. In the case of benzoic acid, the extra carbon atom (i.e., the carboxylic group) could exhibit similar rotation but the much higher acid strength can apparently overcome this effect.

Essentially similar results are obtained when we move further down in the order of decreasing dopant acid strength. In Figure 10, we show spectra of the same gel used in Figure 9 but doped with ethylaniline. Resonances of ethylaniline also reveal sharp

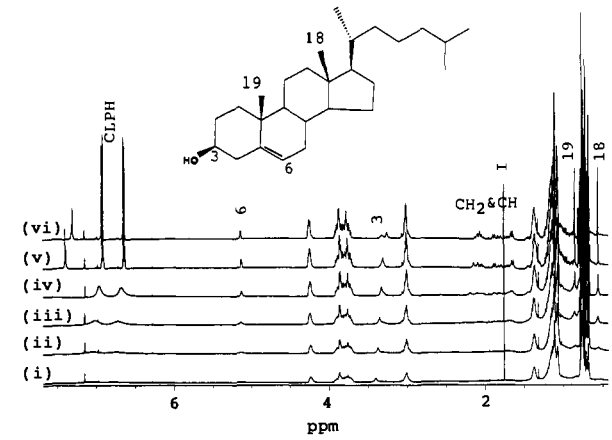

Figure 11. Gel doping with cholesterol. The gel contains 0.16 M 4-chlorophenol, 0.2 M AOT, and 0.04 M cholesterol in 95% CCl_4 and 5% deuteriobenzene solvent. Cholesterol resonances are labeled according to the numbering scheme in the structure shown. The CH_2&CH label includes all the other protons on the fused ring system. Protons of the aliphatic tail are obscured by the AOT tail region resonances (0.65–0.85 ppm and 0.95–1.55 ppm): (i) 20 °C, (ii) 25 °C, (iii) 30 °C, (iv) 35 °C, (v) 40 °C, (vi) 45 °C.

and well-resolved features, indicating that it also does not exist in the motionally restricted portion of the gel matrix but exists in the region with fluid mobility. Essentially identical results were obtained in experiments of gel doping with naphthalene, which is planar and aromatic but is non-hydrogen-bonding. It seems clear that a dopant molecule must be relatively rigid and flat and must have an acidic proton to be incorporated into the motionally restricted region of the gel strand.

Structural Effects, Other Hydrogen-Bonding Agents: Cholesterol. Cholesterol is of considerable interest in mammalian biology because of its suggested role in partitioning at phospholipid cell membranes and subsequent stiffening of biological membranes and its implied role in the deposition of arteriosclerotic plaques in the lumens of blood vessels. Our own interest in cholesterol stems from the observation that it hydrogen-bonds to the AOT head group with an unexpectedly high affinity.[5] In their infrared spectral analysis, Menassa and Sandorfy estimate a cholesterol–AOT binding constant (K) of 11 M^{-1} in CCl_4. This value is comparable to the binding of small chain aliphatic alcohols (e.g., K for isopropyl alcohol of ca. 13 M^{-1}) and is greater than K for long chain alcohols (e.g., K = 7 M^{-1} for hexanol and cyclohexanol). The high K value is quite unexpected for cholesterol with its large molecular size of 19 Å, and the reasons for this anomaly are still unclear.[5] It is illustrative to compare this binding strength to a cresol–AOT binding constant of ca. 200 M^{-1} in isooctane solutions, reported by Magid and co-workers. In CCl_4, the cresol–AOT interaction may be expected to be weaker due to the better solvation properties of CCl_4 compared to isooctane.

The structure of cholesterol is interesting in that it possesses a wrinkled planar structure. It was felt that the presence of a polar hydroxyl group that exhibits some affinity for the surfactant head group, together with the net planar topology, might aid its intercalation of the gel strand. Thus, the 4-chlorophenol gel (0.16 M 4-chlorophenol, 0.2 M AOT in carbon tetrachloride) was prepared and doped with 3-β-hydroxycholesterol to a final concentration of 0.04 M. Proton NMR spectra for this gel were then recorded at different temperatures. Very interestingly, as shown in Figure 11, the cholesterol resonances are indeed dramatically broadened at room temperature, indicating that cholesterol also experiences severe mobility restrictions. The broadening of resonances is evident for all the nuclei in the cholesterol molecule that are associated with the rigid fused ring structure, including the methyl proton resonances at the 18 and 19 positions. The resonances of protons of the aliphatic tail are obscured by the AOT tail proton resonances (0.95–1.55 ppm and

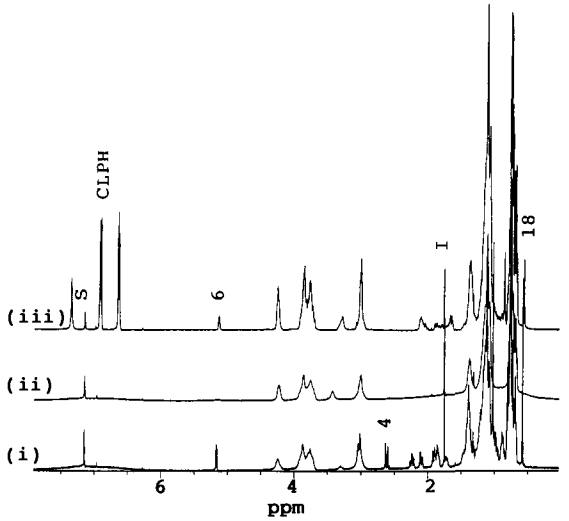

Figure 12. Gel doping with cholestenone. The gel contains 0.16 M 4-chlorophenol and 0.2 M AOT in a 95% CCl_4 and 5% deuteriobenzene solvent. (i) Spectrum of the gel to which 0.04 M 5-cholesten-3-one has been added (20 °C). (ii) The cholesterol-doped gel of Figure 11, trace i (20 °C). (iii) The cholesterol-doped gel, melted by raising the temperature to 45 °C to allow sharpening of cholesterol resonances.

0.65–0.85 ppm), but one may anticipate that this long aliphatic chain may be relatively less restricted. Thus, cholesterol can exist in the gel matrix as an intercalated, motionally restricted species. As with the case of other doped gels, this molecule also falls out of the gel stack upon raising the temperature slightly (or by the addition of trace quantities of water), revealed by a sharpening of resonances at higher temperatures. The critical importance of the hydroxyl group in imparting the stacking ability to the dopant is underscored by the finding that, under identical conditions, 5-cholesten-3-one, the keto- derivative of cholesterol, remains out of the gel stack, as evident from Figure 12.

The interaction of cholesterol with phosphatidylcholine was studied as early as 1977.[12] Yeagle et al., on the basis of $^{31}P\{^1H\}$ nuclear Overhauser enhancement (NOE) effects, conclude that the 3β-OH group of cholesterol hydrogen-bonds to the phospholipid ester carbonyl oxygen atom (but not to either the trimethylammonium or the phosphate group). From ^2H NMR experiments, Dufourc et al. suggest that β-cholesterol acts as a regulatory agent by maintaining the phospholipid bilayer membranes in a liquid-crystalline state.[13] This occurs because, in the presence of cholesterol, the motions of the lipid acyl chains are promoted below the pure lipid's transition temperature (T_c) and motions above the T_c are diminished.

With regard to the interaction of cholesterol with AOT reversed micelles, the exact nature of the interaction is not conclusively established. On the basis of transverse relaxation rates and NOE measurements, Maitra and co-workers[14,15,16] conclude that hydrogen-bonding occurs with the ester carbonyl groups of AOT (but not with the sulfonate), in analogy to the cholesterol–phospholipids study of Yeagle et al.[12] However, the AOT–cholesterol studies are incomplete in the sense that equally compelling evidence of hydrogen-bonding to the sulfonate group of AOT seems to have been ignored. Our own FTIR characterization studies of phenol–AOT interactions did reveal perturbation of the S=O symmetric and asymmetric vibrations in addition to the splitting of the C=O stretching vibrations.[1] We feel that the hydrogen-bonding proton probably interacts with *both* the sulfonate and the carbonyl group closest to it, on the basis of phenol-induced anisotropic effects on the X-proton of AOT subsequent to binding.[2]

Table 1. Summary of Dopants Behavior in Mixed Gels[a]

dopant	intercalation/ stacking	comments
4-cresol	yes	dopant has greater freedom of motion than the gel-forming phenol; readily extruded when heated
2-cresol	yes	dopant has greater freedom of motion than the gel-forming phenol; readily extruded when heated
benzoic acid	yes	dopant has greater freedom of motion than the gel-forming phenol; readily extruded when heated
benzyl alcohol	no	rotation at the $-CH_2-$ bridge
naphthalene	no	not a proton donor
ethylaniline	no	dopant not acidic
cholesterol	yes	large planar topology
5-cholesten-3-one	no	not a proton donor

[a] The gel is formed with (4-chlorophenol + AOT) in CCl_4 at concentrations between 0.1 and 0.2 M (see text for details).

Conclusions

A variety of molecules have been shown to be able to intercalate the gel structure from the fact that their NMR resonances exhibit dramatic broadening. The observations with the dopant species examined in the present work are summarized in Table 1. A primary requirement on the part of an intercalating dopant is, of course, the presence of the proton-donating groups. The finding with gels containing no dopants is that the more acidic the proton donor the stronger the AOT binding and the harder the gel. This is also generally applicable in predicting the stacking abilities of various dopant molecules into a preexisting gel matrix. Furthermore, the hydrogen-bonding proton must be easily accessible to the bulky AOT molecule. More subtle requirements for these dopants to be able to intercalate the phenol aromatic stack include the presence of at least a gross planar topology (as with cholesterol). The hydroxyl group is best located on the same plane as the rest of the molecule, i.e. it needs to be a secondary alcohol.

These findings, we believe, provide important insights toward realizing interesting applications. For example, strongly luminescent gels could be formed with 2-naphthol, and these naphthol gels admit doping with several suitable species. Luminescence quenching in such doped luminescent gels may be explored for possible existence of low-dimensionality energy transfer pathways in these gels. Further, it appears that the gel structure may be used as a template to nucleate synthesis of inorganic nanostructures. These possibilities are currently being explored in this laboratory.

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