Lyotropic Liquid-Crystalline Mesophases of [Zn(H2O)6](NO3)2·C12EO10·CTAB·H2O and [Zn(H2O)6](NO3)2·C12EO10·SDS·H2O Systems

Cemal Albayrak, Asli M. Soylu, and Ömer Dag*

Laboratory for Advanced Functional Materials, Department of Chemistry, and Institute of Material Science and Nanotechnology-UNAM, Bilkent University, 06800, Ankara, Turkey

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The mixture of two surfactants (C12EO10·CTAB and C12EO10·SDS) forms lyotropic liquid-crystalline (LLC) mesophases with [Zn(H2O)6](NO3)2 in the presence of a minimum concentration of 1.75 H2O per C12EO10. The metal ion/C12EO10 mole ratio can be increased up to 8.0, which is a record high metal ion density in an LLC mesophase. The metal ion concentration can be increased in the medium by increasing the CTAB/C12EO10 or SDS/C12EO10 mole ratio at the expense of the stability of the LLC mesophase. The structure and some thermal properties of the new mesophase have been investigated using XRD, POM, FTIR, and Raman techniques.

Introduction

The lyotropic liquid-crystalline (LLC) properties of oligo-ethylene oxide surfactants (CnH2n+1(OCH2CH2)mOH, represented as CnEOm) with water1 and water—oil mixtures2 have been known in the literature for quite some time. Two or three surfactant systems, such as H2O—CTAB—C12EOm, H2O—SDS—C12EOm, and H2O—SDS—CTAB—C12EOm (CTAB is C16H33N(CH3)3+ Br and SDS is C12H25OSO3Na), have also been investigated in their micelle solution phases.3 Many groups also presented the influence of salt ions on the H2O—CnEOm LLC mesophases.4 and lyotropic metallomesogens.4 However, the water—salt—surfactant (WSS) systems are stable only up to certain salt concentrations and depend on the counterion of the salts.5 Later, Dag et al. discovered the presence of a new LLC mesophase that contains a transition-metal salt and oligo(ethylene oxide), TMS—C12EO10, with a relatively high salt concentration.6 In this self-assembly process, the coordinated water molecules, M—OH2, can induce the self-assembly of the CnEOm molecules into LLC mesophases through hydrogen bonding (M—OH2—OCH2CH2) and ion—dipole and ion—ion interactions.6 Note also that the presence of the TMS—surfactant LLC phase has been investigated on TMS—pluronics and lanthanide—CnEOm systems.7

The importance of the TMS—surfactant mesophase is that it can be directly used to produce mesostructured metal oxides.8

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*Corresponding author. Tel: 90-312-2903918. Fax: 90-312-2664068. E-mail: dag@fen.bilkent.edu.tr.


CTAB and between 2.0 (48.7% w/w) and 8.0 (79.2% w/w) in 
\([\text{Zn(H}_2\text{O)}_6](\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\)–SDS. The charged surfactant/
\(\text{C}_12\text{EO}_{10}\) mole ratio has been changed between 0.0 and 1.0 (38.6%
w/w CTAB/(CTAB + \(\text{C}_12\text{EO}_{10}\)) for CTAB and 0.0 and 0.75 
(25.6% w/w SDS/(SDS + \(\text{C}_12\text{EO}_{10}\))) for SDS. The free-water 
content of the mixtures can be reduced to as low as 1.75 H\(_2\)O molecules 
per \(\text{C}_12\text{EO}_{10}\) (4.8% w/w H\(_2\)O/(H\(_2\)O 
concentrations in the media. The \([\text{Zn(H}_2\text{O)}_6](\text{NO}_3)_2\) 
mole ratio is about 35 (50% w/w) in an ordinary H\(_2\)O–\(\text{C}_12\text{EO}_{10}\) 
hexagonal LLC phase.\(^1\) The evaporation of extra water leads to 
the slow crystallization of the salts from the LLC mesophase. However, 
the LLC phase can be recovered after crystallization if samples are 
kept in a humid environment. Note also that even 
\(8[\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\)–CTAB–H\(_2\)O 
is stable over several 
hours of water evaporation (Figure S1A). The LLC mesophase 
is stable in closed vials for several months or longer. It is 
a general trend in both CTAB and SDS systems that the solubility 
of TMS increases with increasing CTAB or SDS amount at the 
expense of the stability of the LLC mesophase.

Figure 1 displays XRD patterns of fresh and aged 
\(6[\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}-0.5\text{CTAB–7H}_2\text{O}\) samples under 
ambient conditions. The diffraction pattern is characteristic of a 3D 
hexagonal LLC mesophase with a unit cell parameter 
a \((100), (002), (101), (102), (103), (112), (203), and (301) planes of the 3D 
hexagonal mesophase. Note also that the plot of \(d\)-spacing values versus \(x\) (where \(d = \pi u x\) and 
\(x = (8/10.667(k^2 + 2hk + k^2)/3h^2)\) is linear with an intercept 
of zero and a slope of 70.2 \(\AA\). However, the XRD pattern of the 
aged sample has four diffraction lines, corresponding to the (100), 
(110), (200), and (210) planes of the 2D hexagonal mesophase 
(Figure 1b). Note that the unit cell parameter \(a\) \((a = 70.2 \AA\) 
that shifts to 63.3 \(\AA\) with water evaporation) of the new mesophase 
is much larger than that of the \([\text{Zn(H}_2\text{O)}_6](\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\) LLC 
\((a = 55.4 \AA\) and the mesostructured silica \((a = 53.1 \AA\) obtained 
using \(\text{C}_12\text{EO}_{10}\) and very much depends on the salt and water 
concentrations in the media. The \([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\)–SDS–H\(_2\)O samples also have similar diffraction patterns at small 
angles (Figure S1B in Supporting Information).

The polarized optical microscopy (POM) image of an aged 
sample shows a fan texture characteristic of a 2D hexagonal 
mesophase (Figure 2). Note that the fan texture exists up 
to an 8.0 salt/\(\text{C}_12\text{EO}_{10}\) mole ratio in both \([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\)–

\(\text{CTAB–7H}_2\text{O}\) samples.

### Table 1. Isotropization temperatures (IT) of the 
\([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\)–CTAB–H\(_2\)O and 
\([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\)–SDS–H\(_2\)O LLC samples with 
various compositions\(^a\)

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<th>Composition</th>
<th>IT (°C)</th>
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<tr>
<td>([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}<em>12\text{EO}</em>{10})–CTAB–H(_2)O</td>
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<tr>
<td>([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}<em>12\text{EO}</em>{10})–SDS–H(_2)O</td>
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<tr>
<td>M(^b)</td>
<td>CTA(^c)</td>
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\(^a\) Number of moles of \(\text{C}_12\text{EO}_{10}\) is 1.0 in all samples. \(^b\) Mole ratios with respect to \(\text{C}_12\text{EO}_{10}\). \(^c\) M = \([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2\). \(^d\) I = insoluble and L = liquid.

C\(_{12}\text{EO}_{10}\)–CTAB–H\(_2\)O and \([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\)–SDS–H\(_2\)O 
systems in a broad range of salt and CTAB concentrations. Interestingly, below 2.0 salt/\(\text{C}_12\text{EO}_{10}\), the 
\([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\)–SDS–H\(_2\)O mixture is insoluble. 
Note that the LLC mesophase of 2.0 salt/\(\text{C}_12\text{EO}_{10}\) is stable in the 
presence of up to a mole ratio of 1/4 SDS/\(\text{C}_12\text{EO}_{10}\) but is 
insoluble in the presence of \(\geq 3/8\) SDS/\(\text{C}_12\text{EO}_{10}\) mole ratios. To investigate 
the thermal properties of the new systems, we have 
recorded their isotropization temperatures (ITs) using a hot stage 
under the POM. The ITs of the new systems are in general low 
compared to that of the \([\text{Zn(H}_2\text{O)}_6]_6(\text{NO}_3)_2-\text{C}_12\text{EO}_{10}\) LLC system\(^c\) 
and decrease with increasing charged surfactants (CTAB or SDS) 
and salt concentrations. Note also that the LLC mesophase 
\(\text{C}_12\text{EO}_{10}\)–CTAB without water is stable at low salt concentrations 
and has relatively higher IT values. (The thermal behavior of the 
new systems will be discussed elsewhere, but a small IT list is 
given in Table 1.) Both systems show similar responses to heating—a 
decreasing trend in IT with increasing salt, water, and 
charged surfactant concentrations; see Table 1.

Figure 3 displays a series of FTIR spectra of the LLC samples, 
obtained from the \(\text{C}_12\text{EO}_{10}\)–CTAB surfactant systems. The spectra were recorded either by spreading a thin 
layer of the LLC
samples on a silicon surface or sandwiching the sample between two silicon wafers (which prevents the evaporation of water). Notice that the nitrate asymmetric stretching region (around 1290–1460 cm⁻¹) has the most intense peaks in the spectra because of the presence of an extensive number of nitrate ions incorporated into the LLC mesophases (details in Supporting Information, Figure S2A). The solvated CTAB molecules display characteristic peaks in the ν-CH regions (2600–2900 cm⁻¹); see Figure S2B. The shoulder at around 2850 cm⁻¹ is also characteristic of a solvated CTAB species. Notice that the difference spectra between the 6.0[Zn(H2O)6](NO3)2-C12EO10-CTAB-7H2O and 6.0[Zn(H2O)6](NO3)2-C12EO10-0.5 CTAB-7H2O samples, where the only change is in the CTAB concentration, clearly show that the CTAB ions are not solvated in the crystalline form in the LLC media. The ν-CO mode of ethylene oxide units of C12EO10 is also very sensitive to its environment. The ν-CO mode, which is observed at 1120 cm⁻¹ in pure C12EO10, shifts to 1110 cm⁻¹ in the presence of water, to 1094 cm⁻¹ in the presence of water and salt ions, and to 1080 cm⁻¹ in the presence of only salt ions. The trend indicates that the strongest interaction is between coordinated water species and ethylene oxide units. The FTIR and Raman spectra of a series of [Zn(H2O)6](NO3)2-C12EO10-SDS-H2O samples were also recorded over a broad range of salt and SDS concentrations. The difference spectra, between the spectra of 5[Zn(H2O)6](NO3)2-C12EO10-0.5SDS-7H2O recorded right after spreading the sample on a silicon wafer and 5, 10, and 15 min after spreading, show changes in the nitrate, sulfate, and ethylene oxide regions (Figure S2C). The most intense peaks of the sulfate headgroup, ν-SO3 asymmetric modes at 1220 and 1253 cm⁻¹, shift to 1178 and 1256 cm⁻¹ in the LLC mesophase, respectively, indicating that the sulfate headgroup of SDS strongly interacts with the positively charged metal species (Figure S2D). Also note that the peak at 954 cm⁻¹ is assigned to the gauche conformer of the ethylene oxide unit that appears in the difference spectra. It indicates that some trans-EO goes to gauche-EO upon water evaporation. The conformational change reduces the thickness of the ethylene oxide hydrophilic shells. This is consistent with the shift of the diffraction lines to higher angles upon water evaporation and it is the likely reason for the phase change from the 3D to 2D hexagonal structure.

Notice that the metal ion concentrations in the new systems, [Zn(H2O)6](NO3)2-C12EO10-CTAB and [Zn(H2O)6](NO3)2-C12EO10-SDS are 2 to 3 times higher compared to that of [Zn(H2O)6](NO3)2-C12EO10 and are comparable to the SiO2/C12EO10 mole ratio (about 6 to 7) in the mesostructured silica. The surfactant molecules mix well in the LLC mesophase to form a charged interface in the hydrophobic alkyl tail and ethylene oxide interface region. The interaction between the charged surfactant and oligo(ethylene oxide) enhances the hydrophobicity of the core (by alkyl tails and hydrophobic force) and the hydrophilicity of the EO shell (by the charged head groups); see schema in Figure 4. The charged surfactants create a positive (CTAB) or negative (SDS) charge at the hydrophobic (alkyl tail)–hydrophilic (ethylene oxide units) interface. In the case of the cationic surfactant, there is an NS⁺ A⁻ M⁺ interaction (where NS⁺ is a micelle of C12EO10-CTA⁺ complex cation, A⁻ is the counteranion, and M⁺ is [Zn(H2O)6]2⁺ or [Zn(H2O)6](O2NO)⁺ ions), and in the case of the anionic surfactant, there is an NS⁻ M⁻ A⁺ interaction (where NS⁻ is a micelle of C12EO10−DS− complex anion), which allows the system to dissolve more TMS at this interface. Both the hydrogen bonding and electrostatic interactions between the charged surfactants and salt ions in the system make the salt−surfactant LLC mesophase stable at very high salt concentrations.

Conclusions

In summary, the surfactant molecules interact with each other in both the hydrophobic core and hydrophilic shell of the assembly to maintain much larger numbers of salt ions in their LLC mesophases. The stable samples require a small number of water molecules in the media. Note that the salt−C12EO10 system becomes liquid in the presence of extra water. However, in the two surfactants systems the free water is necessary to prevent the crystallization of salt ions. The evaporation of water from the media causes a 3D to 2D hexagonal phase change and promotes the crystallization of salt ions. Further studies are required to elucidate the structures and phase behaviors of the new salt−two surfactant LLC mesophases. The LLC mesophases of the other first-row and some second-row TMS in the TMS−C12EO10−CTAB (or SDS)−H2O and TMS−pluronic−CTAB (or SDS)−H2O systems need to be investigated. The new

Figure 3. FTIR spectra of (a) C12EO10, (b) C12EO10-0.5CTAB-H2O, (c) 3[Zn(H2O)6](NO3)2-C12EO10-0.5CTAB-H2O, (d) fresh 6[Zn(H2O)6](NO3)2-C12EO10-0.5CTAB-H2O, and (e) 6[Zn(H2O)6](NO3)2-C12EO10-0.5CTAB-H2O aged for 1 day under ambient conditions (where * indicates the nitrate peaks).

Figure 4. Schematic representation of the assembly of hexagonal mesophase. The core (purple regions) is alkyl tails of the charged and neutral surfactants, the ethylene oxides, and the charged head group of the charged surfactant, and metal ions (blue stars) are in the dark domains.


mesophases with such high metal ion density can be used to produce mesostructured materials that are not possible with current synthesis methods.

**Experimental Section**

The new TMS–C\textsubscript{12}EO\textsubscript{10}–CTAB–H\textsubscript{2}O LLC system is prepared by dissolving 0.475–3.800 g of [Zn(H\textsubscript{2}O)\textsubscript{6}]\textsubscript{2}(NO\textsubscript{3})\textsubscript{2} salt (corresponding to a 1–8 salt/C\textsubscript{12}EO\textsubscript{10} mole ratio) in 0.050–0.800 g of water (corresponding to a 1.75–28 H\textsubscript{2}O/C\textsubscript{12}EO\textsubscript{10} mole ratio), 1.000 g of C\textsubscript{12}EO\textsubscript{10}, and 0.0–0.581 g of CTAB (corresponding to a 0.0–1.00 CTAB/C\textsubscript{12}EO\textsubscript{10} mole ratio) by continuous shaking in closed vials at 50 °C for 1 day and then at 70 °C for another day. For example, the 6[Zn(H\textsubscript{2}O)\textsubscript{6}]\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}–C\textsubscript{12}EO\textsubscript{10}–0.5CTAB–7H\textsubscript{2}O sample contains 2.850 g of [Zn(H\textsubscript{2}O)\textsubscript{6}]\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}, 1.000 g of C\textsubscript{12}EO\textsubscript{10}, 0.290 g of CTAB, and 0.200 g of H\textsubscript{2}O. Similarly, the [Zn(H\textsubscript{2}O)\textsubscript{6}]\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}–C\textsubscript{12}EO\textsubscript{10}–SDS–H\textsubscript{2}O samples were prepared using the same procedure and SDS instead of CTAB. In those, the samples contained 0.950–3.800 g of the [Zn(H\textsubscript{2}O)\textsubscript{6}]\textsubscript{2}(NO\textsubscript{3})\textsubscript{2} salt, 1.000 g of C\textsubscript{12}EO\textsubscript{10}, 0.0–0.460 g of SDS, and 0.05–0.800 g of H\textsubscript{2}O.

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**Supporting Information Available:** XRD patterns for the 8/1 salt/C\textsubscript{12}EO\textsubscript{10} mole ratio of TMS–C\textsubscript{12}EO\textsubscript{10}–CTAB–H\textsubscript{2}O and TMS–C\textsubscript{12}EO\textsubscript{10}–SDS–H\textsubscript{2}O systems, several FTIR and Raman spectra of the TMS–C\textsubscript{12}EO\textsubscript{10}–CTAB and TMS–C\textsubscript{12}EO\textsubscript{10}–SDS systems, and instrumentation. This material is available free of charge via the Internet at http://pubs.acs.org.

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