

Phase Separation in Liquid Crystalline Mesophases of [Co(H₂O)₆]X₂:P65 Systems (X = NO₃⁻, Cl⁻, or ClO₄⁻)

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Transition-metal aqua complex salts [M(H₂O)₆]X₂ (where M is Mn(II), Co(II), Ni(II), Zn(II), or Cd(II) and X is NO₃⁻, Cl⁻, or ClO₄⁻) can be dissolved in triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) copolymers (Pluronic, such as P65) to form homogeneous liquid crystalline (LC) mesophases. However, the [Co(H₂O)₆]X₂:P65 LC mesophases slowly undergo phase separation into a disordered ion-free phase and an ordered ion-rich LC mesophase. The phase separation also takes place in the two-salt systems [Co(H₂O)₆](NO₃):[Co(H₂O)₆](ClO₄)₂:P65 in which the ion-free disordered domains separate out from the initially ordered homogeneous mesophase. The phase separation results in a physical mixture of a hexagonal nitrate-rich and cubic perchlorate-rich LC and disordered ion-free domains in the mixed salt systems. The driving force in the phase separation in the [Co(H₂O)₆]X₂:P65 system is Co(II)-catalyzed aerobic oxidation of P65 into ester and/or other oxidation products. The separation of ions in the [Co(H₂O)₆](NO₃):[Co(H₂O)₆](ClO₄)₂:P65 system is related to the mesostructures of the two-salt systems that are different, hexagonal in the [Co(H₂O)₆](NO₃):P65 system and cubic in the [Co(H₂O)₆](ClO₄)₂:P65 system. There is no visible phase separation in the other transition-metal salt:P65 systems. The phase separation in the [Co(H₂O)₆]X₂:P65 systems can also be eliminated by keeping the mesophase under a N₂ atmosphere.

Introduction

Oligo(ethylene oxide) nonionic surfactants, C_nH_{2n+1}(OCH₂-CH₂)_mOH (represented as C_nEO_m), and triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) copolymers, Pluronic (represented as EO_xPO_yEO_x), form lyotropic liquid crystalline (LLC) mesophases with some transition-metal aqua complex salts,^{1,2} water,^{3,4} and water/oil.⁵ The liquid crystalline (LC) salt:surfactant samples can be prepared by simply dissolving the metal aqua complex salts [M(H₂O)_n]X₂ (where M is a first- or second-row transition-metal ion or a lanthanide and X is NO₃⁻, Cl⁻, or ClO₄⁻ anion) in nonionic surfactants or Pluronic.^{1,2,6–9} The role of coordinated water molecules and the effects of anions on the LC salt:surfactant mesophases have been extensively investigated.^{6–8} The water coordination sphere of the metal ion weakly interacts with the ethoxy groups of the surfactant molecules through hydrogen-bonding (M–OH₂---OCH₂CH₂–), which induces the self-assembly process of the surfactant molecules into LC mesophases. Recently, we have investigated the mesophases of several Pluronic (L64, P65, and P123) in the presence of [M(H₂O)₆](NO₃)₂ (M = Zn(II) and Co(II)) salts.² The salt:Pluronic systems also form a wide range of mesostructures, such as cubic, hexagonal, tetragonal, and lamella depending on the concentration and type of salts.² A similar LC mesophase has recently been observed by Martin et al. in transition-metal chloride salts and cetyltrimethylammonium

chloride surfactant systems. In this, the MX_n⁻ anions form cetyltrimethylammonium salts that display thermotropic LC mesophases at higher temperatures. The interaction between the cetyltrimethylammonium cation and complex metal anion is electrostatic, and therefore, the cetyltrimethylammonium cation and complex metal anion form solid ionic compounds at room temperature (rt).¹⁰ Transition-metal-containing LC mesophases, known as metallomesogens,^{11,12} are important in the field of lyotropic and thermotropic liquid crystals and have been the topic of many review papers.^{13,14}

In the salt:surfactant systems, the solubility of the salts is a key parameter and follows Hofmeister's series.¹⁵ According to Hofmeister's series, (SO₄²⁻ > HPO₄²⁻ > CrO₄²⁻ > CO₃²⁻ > Cl⁻ > Br⁻ > NO₃⁻ > I⁻ > ClO₄⁻ > SCN⁻), anions on the left side of the series are lyotropic and make surfactant molecules more hydrophobic and anions on the right side are hydrotropic and make the surfactant molecules more hydrophilic. However, the origin of the Hofmeister series is still under debate. There are a few models (for instance, one considers the structure of water molecules that are being influenced by the anions as a key parameter for this series) that explain the effect of anions on various systems, such as the cloud point of surfactants, protein folding, LC mesophases, synthesis of colloidal and mesostructured materials, etc.^{16–20} Recently, there have been some developments regarding the experimental insights and molecular understanding

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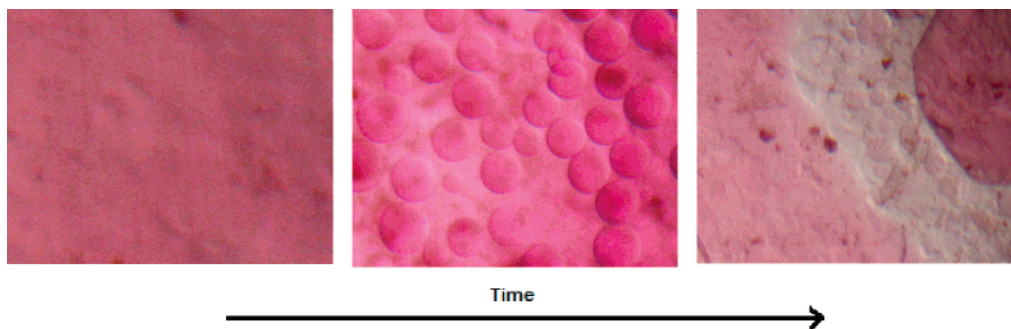


Figure 1. OM images of the fresh and aged samples of $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ (left to right, fresh, 2 days aged, and 2 weeks aged, $400 \times 500 \mu\text{m}$).

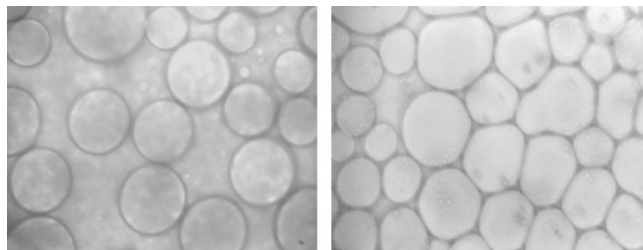


Figure 2. CM images of a 2 days aged $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ sample (left, $180 \times 200 \mu\text{m}$) and 2 days aged perchlorate-rich mixture of $[\text{Co}(\text{H}_2\text{O})_6]\text{X}_2\text{:P65}$ (X is nitrate or perchlorate) (right, $180 \times 200 \mu\text{m}$).

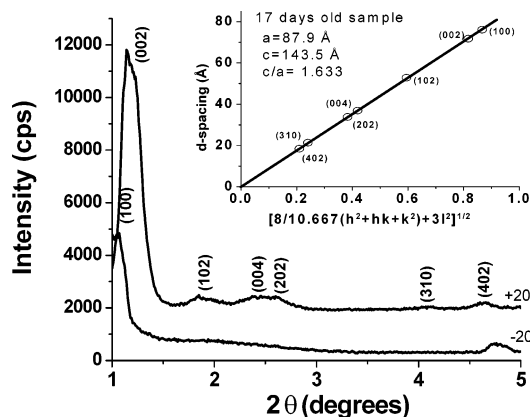


Figure 3. XRD patterns of 17 days aged $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ (2 salt/P65 mole ratio) at two different orientations. The pattern labeled +20 is recorded by rotating the sample by 20° to the right from the normal, and that labeled -20 is recorded by rotating the sample by 20° to the left from the normal. The inset is a plot of the d spacing versus the hkl relationship for a hexagonal structure.

of the Hofmeister series.^{17,18} Guaru et al.²¹ have investigated the conformational changes on the monolayer of octadecylamine over various salt solutions using vibrational sum frequency spectroscopy. They found that the conformational changes follow the Hofmeister series without much influence on the structure of the water molecules underneath.²¹ Sachs and Woolf have studied the dynamics of anion penetration into hydrophobic domains of lipids where hydrotropic anions penetrate more, thereby disrupting the hydrocarbon packing.²² These findings favor the interaction of ions with the surfactant molecules rather than the structure of water.

The LC mesophases of nonionic surfactants and Pluronics have been widely used as templating agents to produce important materials.^{23–25} In a templating process of an inorganic polym-

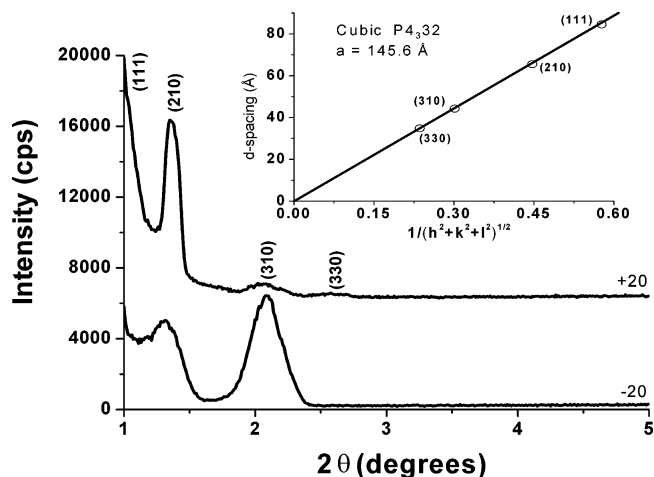


Figure 4. XRD patterns of 17 days aged $[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2\text{:P65}$ (1 salt/P65 mole ratio) at different orientations of the sample with respect to the source–detector axis (+20, rotation of the sample to the right by 20° with respect to the normal; 0, no rotation (normal); -20, rotation by 20° to the left with respect to the normal). The inset is a plot of the d spacing obtained from the above three diffraction lines versus $1/(h^2 + k^2 + l^2)^{1/2}$.

erization reaction, the surfactant molecules undergo conformational changes similar to those of the LC mesophases in various salt systems. Understanding the formation and stability of the LC mesophases of salt:surfactant systems is important for producing new functional materials.

Tanaka et al. have investigated a phase separation from a lyotropic LC system of triethylene glycol mono-*n*-decyl ether (C_{10}EO_3) and water.²⁶ The ordered (lamellar) phase, L_α , and a disordered (sponge) phase, L_3 , coexist in a certain region of the phase diagram of $\text{C}_{10}\text{EO}_3/\text{H}_2\text{O}$. The homogeneous lamellar mesophase of $\text{C}_{10}\text{EO}_3/\text{H}_2\text{O}$ undergoes phase separation upon heating to the coexistence region and results in three different morphologies (cellular, network, and droplet structures) depending on the heating rate and concentration ($\text{C}_{10}\text{EO}_3/\text{H}_2\text{O}$ ratio).²⁶ Transition-metal-based lyotropic metallomesogens and metalomesogens in general have been reviewed in detail by Donnio¹³ and Binnemans,¹⁴ respectively. Here we report a phase separation that is induced by ions in salt:Pluronic LC systems, in which the ions become concentrated in ordered LC regions. The phase separation, phase-separation-induced ordering, and molecular origin of the phase separation in a salt:Pluronic LC system were

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Table 1. (*hkl*) Planes and *d* Spacing (Å) Values Obtained from the XRD Patterns of the Aged (17 days) Samples of $2[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ and a Fresh Sample of a Mixed Salt System ($1[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2 + 1[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2:\text{P65}$)

$2[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ (aged 17 days)		$1[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2:\text{P65}$ (aged 17 days)		$(1[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2 + 1[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2):\text{P65}$ (fresh)			
(<i>hkl</i>)	<i>d</i> spacing (Å)	(<i>hkl</i>)	<i>d</i> spacing (Å)	(<i>hkl</i>)	<i>d</i> spacing (Å)	(<i>hkl</i>)	<i>d</i> spacing (Å)
(100)	76.1	(111)	84.5	(111)	74.0	(311)	38.8
(002)	71.8	(210)	65.5	(200)	63.5	(321)	34.2
(102)	52.9	(310)	44.2	(210)	56.3	(400)	32.0
(004)	36.9	(330)	34.8	(211)	51.4	(521)	22.6
(202)	33.9			(300)	42.2		
(310)	21.4						
(402)	18.5						

investigated using optical microscopy (OM), confocal microscopy (CM), micro Raman spectroscopy, FTIR spectroscopy, and X-ray diffraction (XRD) techniques.

Experimental Section

Materials and Sample Preparation. The Pluronic P65 ($\text{PEO}_{20}\text{-PPO}_{30}\text{PEO}_{20}$, $M_{\text{av}} = 3500$) was generously donated by BASF Corp. and used without further treatment. The transition-metal salts were obtained from Aldrich and/or Fluka. The binary mixtures of salt:P65 were prepared by dissolving an appropriate amount of ground $[\text{M}(\text{H}_2\text{O})_6]\text{X}_2$ salts ($M = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Zn^{2+} , or Cd^{2+} and $X = \text{NO}_3^-$, ClO_4^- , or Cl^-) in P65 (the salt/P65 mole ratio was varied between 0.1 and 7.0) through heating the closed vial in a water bath at around 70 °C overnight. This ensures a homogeneous mixture for each composition. The ternary samples $\text{H}_2\text{O}:\text{salt}:\text{P65}$ were prepared by first dissolving an appropriate amount of $[\text{M}(\text{H}_2\text{O})_6]\text{X}_2$ salt in 1–3 g of water and then adding 1.00 g of P65 to this clear solution, where the salt/P65 mole ratio has been varied between 0.1 and 7.0. The resulting mixture is homogenized by heating the mixtures at 50 °C for 30 min in a water bath in sealed vials. Note that there is no effect of heating if the reaction vessel is sealed and the mixture is liquid at high water contents. The slow evaporation of the excess water gives the binary salt:surfactant LC mesophase.

Characterization. The OM images were obtained in transmittance mode on a Meije Techno ML9400 series polarizing microscope with transmitted light illumination. The XRD patterns of the LC samples, packed into 0.5 or 0.2 mm glass sample holders or glass plates, were recorded on a Rigaku Miniflex diffractometer using a high-power Cu K α source operating at 30 kV/15 mA and a Scintillator NaI(Tl) detector with a Be window. The micro Raman spectra were recorded on a LabRam confocal Raman microscope with a 300 mm focal length. The spectrometer is equipped with a HeNe laser operated at 20 mW, polarized 500/1 with a wavelength of 632.817 nm, and a 1024×256 element CCD camera. The signal collected was transmitted through a fiber optic cable into a spectrometer with a 1800 or 600 g/mm grating. The Raman spectra were collected by manually placing the probe tip near the desired point of the sample on a glass slide. The same systems were also used to record the confocal microscopy images. FTIR spectra were recorded with a Bruker Tensor 27 FTIR spectrometer. A high-sensitivity DLATGS detector was used with a resolution of 4 cm^{-1} and 64 scans for all the samples. The FTIR spectra were recorded as thin films on a single Si(100) wafer.

Results and Discussion

The samples investigated in this work were prepared by dissolving $[\text{M}(\text{H}_2\text{O})_6]\text{X}_2$ (where M is Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , or Cd^{2+} and X is NO_3^- , Cl^- , or ClO_4^-) in P65, $\text{EO}_{20}\text{PO}_{30}\text{EO}_{20}$ (EO is $-\text{OCH}_2\text{CH}_2-$ and PO is $-\text{OCH}(\text{CH}_3)\text{CH}_2-$) with salt/Pluronic mole ratios of between 0.1 and 7.0. Some of the samples were prepared in the presence of excess water to speed the mixing and homogenizing process (by first dissolving the salts in water, then adding P65, and then slow evaporation of excess water). Note that it is also possible to use ethanol as a cosolvent. The

LC phase of most nitrate ($[\text{M}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$) samples are homogeneous up to a 7.0 salt/P65 mole ratio. However, the perchlorate ($[\text{M}(\text{H}_2\text{O})_6](\text{ClO}_4)_2:\text{P65}$) systems can be homogenized up to a 4.0 salt/P65 mole ratio, and the chloride ($[\text{M}(\text{H}_2\text{O})_6]\text{Cl}_2$) salts are insoluble in P65 (except if M is Co^{2+})⁸ or partially soluble and crystallize out in time.²⁷ It is generally true that the nitrate salts are more soluble in the LC mesophase than the perchlorate salts. The samples are liquid-like at low concentrations (0.1–1.5 salt/P65 mole ratios in nitrates and 0.1–1.0 in perchlorates) and do not diffract at small angles (2θ between 1° and 5°). However, the Co^{2+} samples with lower salt concentrations (less than 1 salt per P65) also diffract at small angles upon several days of aging, indicating a formation of LC mesophases over time.

The homogeneous mixtures of $[\text{Co}(\text{H}_2\text{O})_6]\text{X}_2:\text{P65}$ samples slowly undergo phase separation upon aging. Figure 1 shows OM images of the same sample of $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ with a 2 salt/P65 mole ratio at different points in the aging process. Also note that the aged samples consist of two domains, transparent pink-colored and transparent colorless, in the $[\text{Co}(\text{H}_2\text{O})_6]\text{X}_2:\text{P65}$ systems. The OM and CM images show more details where the colored regions consist of large colored domains (a few millimeters) and highly spherical microdomains (a few ten micrometers) in the $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ systems, Figures 1 and 2. The microdomains slowly grow and merge into larger domains over time, leading to a phase separation into ion-rich and ion-free regions. Note also that if the LC samples of $[\text{Co}(\text{H}_2\text{O})_6]\text{X}_2:\text{P65}$ are kept under a N_2 atmosphere, there is no visible phase separation but there is an enhanced phase separation under an O_2 atmosphere. Moreover, the LC mesophases of other transition-metal salts with P65 do not undergo phase separation.

The mesophases were further investigated by using a small-angle X-ray diffraction method. Note that the salt:P65 samples, regardless of salt type, are oriented as determined from the XRD measurements by placing the sample holder with different angles along the source–sample holder–detector axis. Figures 3 and 4 show the XRD patterns of the $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ and $[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2:\text{P65}$ samples after 17 days of aging, respectively. Note that the XRD patterns of fresh samples of $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ (2–7 salt/P65 mole ratio) usually display one or two diffraction lines at small angles.² However, with aging, in the early stages the diffraction line(s) disappear (most likely due to phase separation), and with further aging, they reappear with as many as seven lines in the $2\theta = 1\text{--}5^\circ$ range, Figure 3 and Table 1. These lines can be indexed to diffraction planes of a 3D hexagonal, $P6_3/mmc$ space group with unit cell parameters $a = 87.9 \text{ \AA}$ and $c = 143.5 \text{ \AA}$ (with $c/a = 1.634$).

The metal chlorides are in general insoluble in P65, except cobalt chloride. Upon dissolving $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$, the chloride

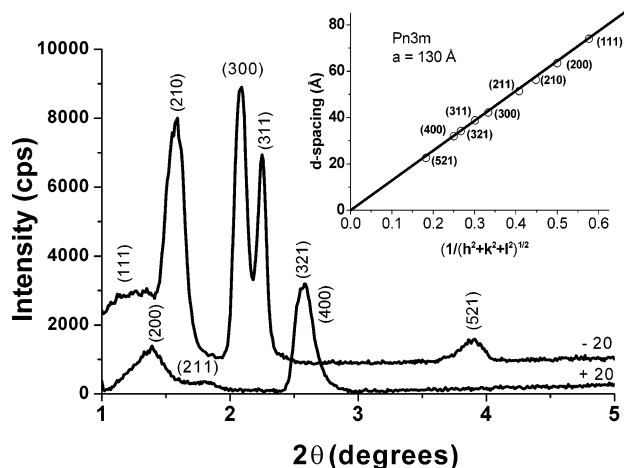


Figure 5. XRD patterns of a fresh $[1[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 + 1[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2]:\text{P65}$ (total 2 salt/P65 mole ratio) mesophase at two different orientations. The inset is a plot of the d spacing versus the hkl relation for a cubic structure.

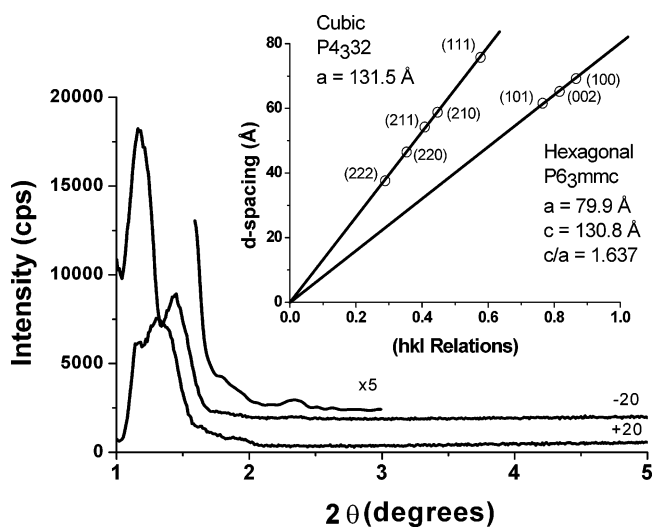


Figure 6. XRD patterns of the same mixture in Figure 5 at two different orientations after 1 day of aging. The inset shows a plot of the d spacing versus the hkl relation for cubic and hexagonal structures.

ions undergo a ligand-exchange reaction and form an equilibrium among the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]$, and $[\text{CoCl}_4]^{2-}$ (blue-colored) complex species⁸ in P65. The structure and phase separation in the $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2:\text{P65}$ system are similar to those in the $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ system. Therefore, they will not be further discussed in this paper. The XRD pattern of the $[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2:\text{P65}$ sample (1 salt/P65 mole ratio) shows diffraction lines that can be indexed to planes of a cubic mesophase with a space group of $P4_332$ and a unit cell parameter $a = 145.6$ Å, Figure 4 and Table 1. The mesophase is gel-like (dense) in the perchlorate salt systems at lower salt concentrations and becomes very fluidic at higher perchlorate concentrations.

The mixed salt systems are either cubic or hexagonal depending on the nitrate/perchlorate ratio, the nitrate-rich samples are hexagonal, and the perchlorate rich samples are cubic. Figures 5 and 6 show the diffraction patterns of a fresh and aged sample of mixed salt:P65 ($1[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2/1[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$, total 2 salt/P65 mole ratio) samples, respectively. The diffraction pattern of the fresh sample displays up to nine diffraction lines that originate from a cubic, $Pn3m$ space group and gives a unit cell parameter $a = 130$ Å; see Table 1. However, with aging (phase separation), the XRD pattern changes and can no longer

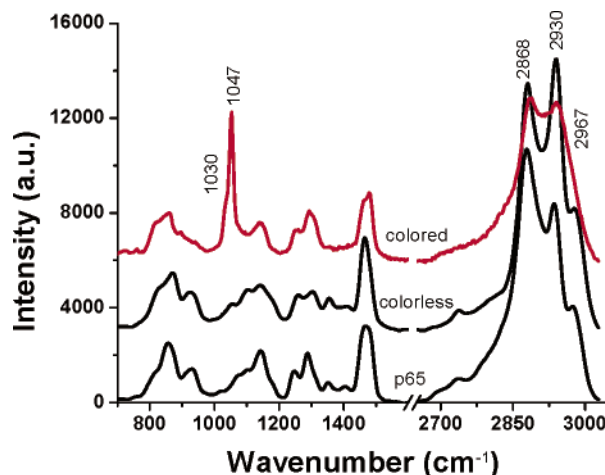


Figure 7. Micro Raman spectra of colorless and colored regions of 17 days aged $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ (2 salt/P65 mole ratio) and pure P65.

be indexed to the $Pn3m$ space group. The pattern of the aged samples (17 days) consists of a pattern of a physical mixture of both hexagonal and cubic mesophases, Figure 6. Most likely the perchlorate and nitrate ions also undergo separation during the phase separation process. As a result, the perchlorate-rich areas are cubic with a space group of $P4_332$ (the same as a pure perchlorate system) and the nitrate-rich domains are 3D hexagonal (the same as a pure nitrate system); see Figure 6.

In microdomains, the larger domains and colorless parts of the samples were further analyzed using micro Raman and FTIR spectroscopy to elucidate the molecular nature of the phase separation. We found that the microdomains and large colored parts of the samples have very similar Raman spectra. However, the colorless regions show drastic changes. Figure 7 shows the Raman spectra of a $2[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ system in both colored and colorless domains with a spectrum of a pure P65 for comparison purposes. The top spectrum is obtained from the colored region showing nitrate-related peaks at 1045 and 1030 cm^{-1} due to the symmetric stretching of free and coordinated nitrate ions, respectively. The coordination of nitrate ions with the metal ion in nonionic surfactant/salt and pluronic/salt LC systems has been extensively discussed in our previous papers.^{6–8} Notice also that the middle spectrum does not display any signals due to the nitrate ion, indicating that the colorless region has nitrate ions below our detection limit.

The mixed salt systems were also monitored over time using micro Raman spectroscopy. To elucidate the structure and determine the compositions of the microdomains, the Raman spectra were recorded in even smaller regions by focusing the laser beam over the spherical, distorted spherical, and nonspherical regions of the samples. Figure 8 shows the Raman spectra of a fresh and aged sample of $1[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2/1[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$. The peaks at 1030 and 1047 cm^{-1} due to the coordinated and free nitrate ions, respectively, and 928 cm^{-1} due to the symmetric stretching of perchlorate ion were monitored to follow the separation of ions in the mixed systems. The intensity ratio $I_{928}/I_{(1030+1047)}$ in 1/1 perchlorate/nitrate in all regions of a fresh sample is about 2.57. Notice that the intensity ratio $I_{928}/I_{(1030+1047)}$ drastically changes from domain to domain, not maintaining the same ratios as in their fresh counterparts. Intensity alteration of the nitrate and perchlorate Raman signals also indicates the separation of nitrate and perchlorate ions in the $(2-x)[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2/x[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2:\text{P65}$ system. The intensity alteration of the perchlorate- and nitrate-related Raman peaks correlates well with the observations from the XRD patterns

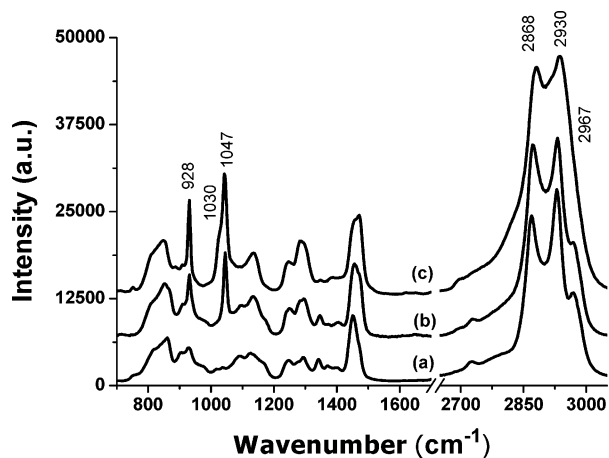


Figure 8. Micro Raman spectra of the mixed salt system (1.0- $[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 + 1.0[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$):P65: (a, c) 17 days aged sample of the ion-free and ion-rich regions, respectively, (b) fresh sample before phase separation.

of the mixed salt samples that diffract two sets of diffraction patterns upon phase separation. The nitrate-enriched domains form a hexagonal mesophase, whereas perchlorate-enriched domains form a cubic mesophase.

The $\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$ stretching Raman modes also respond to the phase separation. Notice that the sharp signals at 2868, 2930, and 2967 cm^{-1} observed in the fresh sample get broader in the ion-rich regions (2979 and 2936 cm^{-1}) and become even sharper and more intense in the ion-free region in the aged sample, indicating interaction between the ions and P65, Figures 7 and 8. The peaks at 2868 and 2930 cm^{-1} are due to the CH_2 and CH_3 groups of P65, respectively, and respond to the concentration of the ions in the medium. The intensity ratio I_{2868}/I_{2930} of these two peaks decreases with increasing salt concentration in the medium, most likely due to changes in the conformation of the EO and PO units of P65. Further studies are required to understand the effect of the ions on the conformation of the P65 in both the ordered and disordered regions.

The FTIR spectra of thin films of $[\text{M}(\text{H}_2\text{O})_6]\text{X}_2\text{:P65}$ samples were recorded on a silicon wafer, Figures 9 and 10. Note that the IR samples are much thinner than both the XRD and Raman samples and the phase separation takes place in a shorter period. Figure 9A displays the IR spectra of a pure P65 and $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ at various conditions. The spectra of the $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ samples change with aging, and two new peaks at 1723 with a shoulder at 1740 and 1184 cm^{-1} appear and eventually dominate the spectra of the $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ samples, Figure 9. Those peaks at 1723 and 1184 cm^{-1} are characteristic and also appear in the spectra of the $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2\text{:P65}$ and $[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2\text{:P65}$ samples under ambient conditions.

Note also that the phase separation does not take place in the $[\text{M}(\text{H}_2\text{O})_6]\text{X}_2\text{:P65}$ (where M is Mn^{2+} , Cd^{2+} , Zn^{2+} , or Ni^{2+}) mesophases at rt and if the $[\text{Co}(\text{H}_2\text{O})_6]\text{X}_2\text{:P65}$ samples had been kept under a N_2 atmosphere, Figures 10 and 9A, respectively. Thus, the phase separation is a function of the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Co}(\text{H}_2\text{O})_{6-n}(\text{X})_n]^{(2-n)+}$ complex ions, air, and temperature (faster at higher temperatures). The peaks at around 1723–1740 and 1184 cm^{-1} are characteristic of ester groups that most likely form during aerobic oxidation of ether groups.²⁸ Figure 9B shows the IR spectra of colored and colorless regions of a $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ sample after phase separation. The spectrum of the colored region is dominated by the nitrate-related peaks (indicating enrichment of the ions, consistent with Raman data), whereas

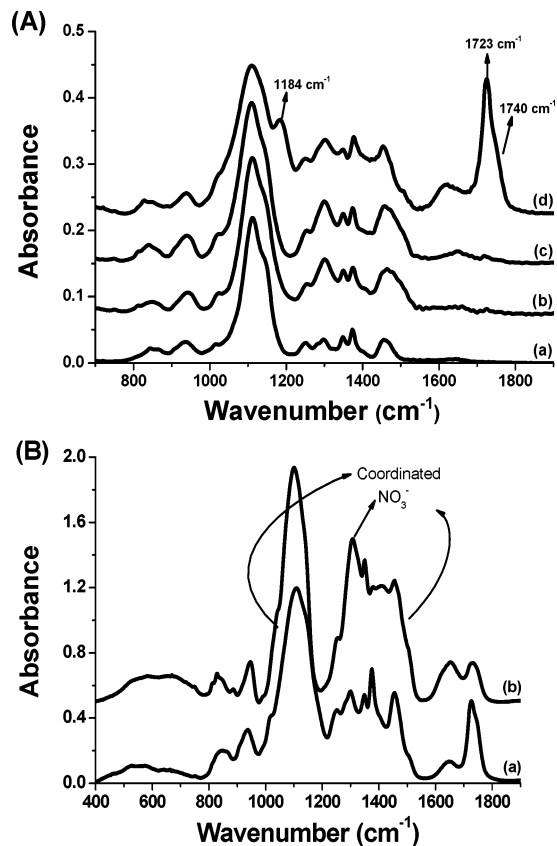


Figure 9. FTIR spectra of (A) (a) P65 and (b–d) $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ (with a salt/P65 mole ratio of 3) [(b) fresh, (c) 5 days aged under N_2 , and (d) 5 days aged under ambient conditions] and (B) colorless (a) and colored (b) regions of $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ (with a salt/P65 mole ratio of 3) after phase separation.

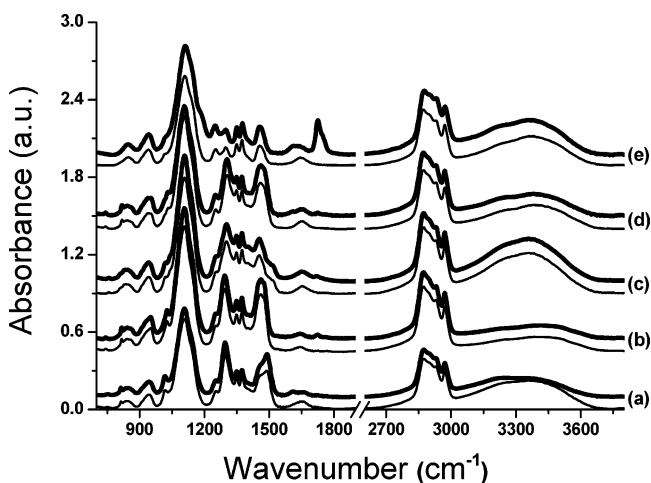


Figure 10. FTIR spectra of fresh (thin lines) and 5 days aged (thick lines) $[\text{M}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{:P65}$ with a 3 salt/P65 mole ratio [M is (a) Zn^{2+} , (b) Cd^{2+} , (c) Ni^{2+} , or (d) Mn^{2+}] and (e) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2\text{:P65}$ with a 3 salt/P65 mole ratio.

the colorless region displays intense peaks at 1723 and 1184 cm^{-1} (indicating a high concentration of oxidized species). Therefore, there is a one to one correlation between the IR peaks (at 1184, 1723, and 1740 cm^{-1}) and the phase separation.

Moreover, on the basis of our observations, we suggest the following mechanism that could be effective in the P65 oxidation and phase separation processes. The sharp and intense diffraction lines in the fresh samples suggest that the fresh samples are ordered and homogeneous and consist with one phase (otherwise one would observe relatively broader and weak XRD line(s) in

the fresh samples). Rather, over time, microdomains appear and grow into larger domains. Notice that, during the aging process, the sharp diffraction line(s) disappear with the formation of disordered microdomains, and re-form upon further aging (with the growth of larger LC domains), indicating that the phase separation starts randomly in the overall sample and leads to ordered (well diffractions) and disordered domains with the separation. Note that the separation is even slower in the samples with a higher salt concentration and relatively faster in low salt concentrations and low humidity conditions (separation is faster if the samples are kept under a dry air or an O₂ atmosphere). At higher salt concentration, the concentration of water molecules (both free and coordinated, the band at around 1646 cm⁻¹) is also high, but low salt concentration and low humidity (under dry air) result in an enhanced Co²⁺-(OCH₂CH₂O)_x interaction. Most likely there is also an equilibrium between Co²⁺-OH₂---(OCH₂CH₂)_x and Co²⁺-(OCH₂CH₂O)_x species. The equilibrium favors the Co²⁺-(OCH₂CH₂O)_x species in dry atmospheres and higher temperatures due to evaporation of coordinated water molecules. The chelating effect of the ethoxy groups (act as multidentate ligands) may stabilize the Co³⁺ ion that forms by creating an O₂⁻ radical. However, O₂⁻ radicals attack and convert the ethoxy groups into ester group(s) by regenerating the Co²⁺ ion. We believe an aerobic and Co²⁺-catalyzed oxidation of P65 into some form of esters and/or other oxidation products²⁸ in the [Co(H₂O)₆]X₂:P65 LC systems drives the phase separation. Most likely the oxidized organic species are more hydrophobic compared to P65, do not undergo conformational changes, and self-assemble into LC mesophases with the help of the [Co(H₂O)₆]²⁺ or [Co(H₂O)_{6-n}(X)_n]⁽²⁻ⁿ⁾⁺ ions (where X is NO₃⁻ or Cl⁻). Therefore, the new species force the continuous LC mesophase of [Co(H₂O)₆]X₂:P65 to break into ordered and disordered regions over time. Note also that the ordered LC regions are more hydrophilic than the ion-free regions. Therefore, the salt ions concentrate in the LC ordered domains of the samples. However, further studies are required to understand the detailed

mechanism in the P65 oxidation, phase separation, separation of ions, etc.

Conclusion

In summary, our observations indicate that the mixtures of some transition-metal salts and P65 form homogeneous lyotropic LC systems with a broad salt/pluronic mole ratio. However, the LC mesophase of [Co(H₂O)₆]X₂:P65 (where X is NO₃⁻, Cl⁻, or ClO₄⁻) undergoes phase separation into more ordered LC ion-rich and disordered ion-free domains over time in ambient conditions. In this process, Co(II) species play an important role that is most likely the catalytic and aerobic oxidation of some of the P65 molecules in the medium. The oxidized P65 species do not form an LC mesophase with the metal ion species. The phase separation also causes a separation of ions in the mixed salt:P65 ([M(H₂O)₆](NO₃)₂: [M(H₂O)₆](ClO₄)₂:P65) systems, leading to nitrate- and perchlorate-rich ordered microdomains with aging. The ion-Pluronic interactions in mixed salt systems influence the hydrophilic/hydrophobic balance of the mesophase and lead to the separation of ions. The hydrophilicity of the medium is determined by the anion, a fact which supports our previous observations in various salt/surfactant systems. However, further spectroscopic studies are required to understand the effect of various ions on the conformational changes of the pluronics in the salt:Pluronic systems and the oxidation mechanism of P65. These studies will further the molecular understanding of the observed unusual phenomena.

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