

Spectroscopic Investigation of Nitrate–Metal and Metal–Surfactant Interactions in the Solid $\text{AgNO}_3/\text{C}_{12}\text{EO}_{10}$ and Liquid-Crystalline $[\text{M}(\text{H}_2\text{O})_n](\text{NO}_3)_2/\text{C}_{12}\text{EO}_{10}$ Systems

Ömer Dag,* Olga Samarskaya, Cenk Tura, Ahmet Günay, and Özgür Çelik

Department of Chemistry, Bilkent University, 06800 Ankara, Turkey

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Interactions of the nitrate ions in various metal nitrate salts with $\text{C}_n\text{H}_{2n+1}(\text{CH}_2\text{CH}_2\text{O})_m\text{OH}$ (C_nEO_m)-type nonionic surfactants have been investigated both in the solid and in the liquid-crystalline (LC) systems. In the ternary system, the mixture of salt/water/ C_nEO_m has a mesophase up to a certain concentration of salt, and the nitrate ions in this phase are usually in a free-ion form. However, upon the evaporation of the water phase, the nitrate ion interacts with the metal center and coordinates as either a bidentate or unidentate ligand. It is this interaction that makes the AgNO_3 ternary system undergo a phase separation by releasing solid $\text{Ag}(\text{C}_n\text{EO}_m)_x\text{NO}_3$ complex crystals. In contrast, the salt/surfactant systems maintain their stable LC phases for months. Note also that the salt/surfactant systems consist of transition-metal aqua complexes in which the coordinated water molecules play a significant role in the self-assembly and organization of the nonionic surfactant molecules into an LC mesophase. Throughout this work, Fourier transform infrared spectroscopy has been extensively used to investigate the interactions of the nitrate ions with a metal center and the metal ions with the surfactant molecules. Polarized optical microscopy and X-ray diffraction techniques have been applied to investigate the nature of the crystalline and LC phases.

Introduction

The studies of the interactions between ions and surfactant molecules or polymers in the liquid-crystalline (LC) micellar solutions of surfactants or ion-conducting polyelectrolyte systems are important areas of modern science. Because the ion–ion interactions (as free ions, ion pairs, or aggregates) and ion–surfactant or ion–polymer interactions determine the physical properties of the polyelectrolytes, it is important to understand the ion–ion and ion–host interactions at a molecular level. The reason many electrolyte systems cannot be used as ion-conducting media is that these interactions usually produce a crystalline host or ion pairs and aggregates of the interested ions.^{1–5} The influence of these ions in the LC phase and cloud point of oligo(ethylene oxide)-type nonionic surfactants have also been extensively studied.^{6–9} For example, LiCF_3SO_3 and AgNO_3 salts^{10–12} can be dissolved in the oligo(ethylene oxide) surfactant, $\text{C}_{12}\text{H}_{25}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{OH}$ ($\text{C}_{12}\text{EO}_{10}$), without disturbing the LC phase of 50% (w/w) $\text{H}_2\text{O}/\text{C}_{12}\text{EO}_{10}$. However, at a higher salt concentration (ca. >0.8–1.0 salt/surfactant mole ratio), either the LC phase collapses or a phase separation

(crystallization of the salt) takes place. Therefore, the surfactant–salt interaction (through the surfactant–cation and cation–anion interactions) plays a very important role in the stabilization of the LC phase.

Çelik and Dag have recently demonstrated that the mixtures of $\text{C}_{12}\text{EO}_{10}$ and $[\text{M}(\text{H}_2\text{O})_n](\text{NO}_3)_2$ -type metal salts in various ratios have an LC phase.¹³ To observe this new system, the salts of transition metals were dissolved and homogenized in the pure C_nEO_m -type nonionic surfactants. Unlike in the salt/water/ C_nEO_m system, the metal-ion concentration can be increased up to a 6.5 salt/surfactant mole ratio.¹³ Note also that this corresponds to a 62.8% (w/w) salt/surfactant ratio. Upon mixing, the resulting phase is transparent and takes the color of the transition-metal ion. However, in these new salt/surfactant systems and AgNO_3 in 50% (w/w) water/surfactant ternary systems, the nitrate-ion–metal and metal–surfactant interactions are not well understood.

Ion binding and the effects of ions on the cloud point of similar surfactants in the LC phase and dilute solutions are challenging problems discussed in the literature.^{6–9} It is well-known that the solubilities of nonionic surfactants are under the influence of inorganic salts. The effects of inorganic additives were first studied almost a century ago by Hofmeister,¹⁴ and it was found that the solubility of the surfactant in water decreases with the electrolyte in the order of $\text{SO}_4^{2-} > \text{HPO}_4^{2-} > \text{CrO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$. This is known as the Hofmeister series. However, the origin of this series has not yet been well understood.^{6–8} There are many studies on the experimental and theoretical aspects of ion binding in the literature.^{6–9} It is commonly addressed that the interactions of the anions are more important than those of the metal ions in such systems. However, the main consensus is that the origin of the Hofmeister series is not yet clear.

* To whom correspondence should be addressed. Fax: 90 312 266 4579. Telephone: 90 312 290 3918. E-mail: dag@fen.bilkent.edu.tr.

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In coordination chemistry, it is well-known that the interaction of a counteranion and a metal ion in a solution of the transition-metal salts is usually of a coordinative type. For example, a nitrate ion can coordinate with the transition-metal ion through either one of its oxygen atoms (unidentate) or two of its oxygen atoms (bidentate). This interaction lowers the symmetry of the free nitrate ion from the D_{3h} to the C_{2v} point group; therefore, the degeneracy of the IR-active E' modes of the free nitrate ion (asymmetric and bending modes) is lifted and split into two nondegenerate IR-active B_2 and A_1 modes. Therefore, two peaks are observed around the free-nitrate-ion-frequency regions in the IR spectrum. The splitting energy provides information regarding the type of coordination and is relatively smaller in the unidentate coordination than in the bidentate coordination in similar complexes.¹⁵ Accordingly, the following is observed in the IR spectra of the nitrated metal complexes: (1) splitting of the in-plane bending mode (E' , ν_4) near the 700–760- cm^{-1} region, (2) combination bands (as a result of $\nu_1 + \nu_4$, the symmetric stretching and in-plane bending modes) at around the 1700–1800- cm^{-1} region (the splitting energy in the unidentate coordination is around 6–20 cm^{-1} and in the bidentate coordination is relatively larger around 25–60 cm^{-1}), (3) splitting of the asymmetric stretching mode of the nitrate ion giving two peaks at around the 1360- cm^{-1} region with a relatively larger splitting energy, which also senses the coordination type, and (4) IR-inactive symmetric stretching mode at around 1000–1050 cm^{-1} becoming active.

Here, we demonstrate an experimental example of the ion-binding ion-surfactant and ion-ion interactions in the LC phases of the $\text{H}_2\text{O}/\text{AgNO}_3/\text{C}_{12}\text{EO}_{10}$ (by the evaporation of the water content or aging of the LC phase) and salt/ $\text{C}_{12}\text{EO}_{10}$ {salts used in the systems studied are $[\text{Mn}(\text{H}_2\text{O})_4](\text{NO}_3)_2$, $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$, and $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ } systems. To explore and further elucidate the systems described above, polarized optical microscopy (POM), Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) techniques were used extensively.

Experimental Section

The samples used throughout this work were prepared using the methods previously described.^{11,13} The LC phases of the salt/surfactant and salt/water/surfactant systems were first identified by POM. The POM images were recorded in the transmission mode on Meije Techno ML9400 and Stereo Microscope Stemi 2000 microscopes using convergent white light between parallel and crossed polarizers. The XRD patterns were obtained on a Rigaku Miniflex diffractometer using a high-power $\text{Cu K}\alpha$ source operating at 30 kV/15 mA. The FTIR spectra were recorded in the transmittance mode using a Bomem Hartman MB-102 model FTIR spectrometer.

Results and Discussion

Each sample was characterized using POM and XRD techniques before further investigations. The POM images of both the salt/water/surfactant and salt/surfactant systems of the transition-metal nitrates display a typical fan texture, which corresponds to a hexagonal mesophase (Figure 1A). The XRD patterns were recorded from the samples in the solid phase of the $\text{AgNO}_3/\text{H}_2\text{O}/\text{C}_{12}\text{EO}_{10}$ system and the water-free LC phase of the transition-metal aqua complexes. A set of XRD patterns of the $[\text{Mn}(\text{H}_2\text{O})_4](\text{NO}_3)_2/\text{C}_{12}\text{EO}_{10}$ system with various salt/sur-

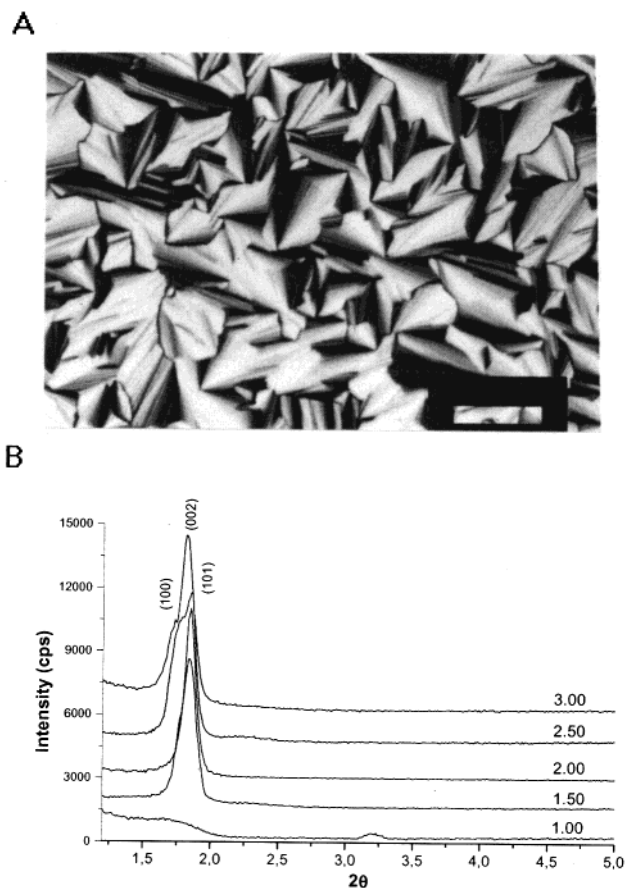


Figure 1. (A) Typical POM image of the LC phase of a $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2/\text{C}_{12}\text{EO}_{10}$ system (note that the $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2/\text{C}_{12}\text{EO}_{10}$ system forms a two-dimensional hexagonal phase). (B) XRD patterns of the $[\text{Mn}(\text{H}_2\text{O})_4](\text{NO}_3)_2/\text{C}_{12}\text{EO}_{10}$ system with various mole ratios (shown on the patterns).

factant mole ratios is shown in Figure 1B. The XRD patterns of the samples display three diffraction lines in the 1.7–2.2° 2θ region corresponding to the (100), (002), and (101) lines of the $P6_3mmc$ space group of the three-dimensional hexagonal LC mesophase (Figure 1B). The phase characterizations and thermal properties of the binary systems have been published previously.¹³ This article focuses on the metal–nitrate and metal–surfactant interactions on a molecular level through the use of FTIR spectroscopy.

With this purpose in mind, the LC phase of the AgNO_3 system was obtained at various concentrations of the AgNO_3 salt, which was dissolved in a minimum amount of water and then mixed to form a 50% (w/w) water/surfactant mixture.^{11,12} However, the LC phase is not stable and is subject to aging at higher $\text{AgNO}_3/\text{C}_{12}\text{EO}_{10}$ mole ratios in which the mixtures release white, solid-crystalline particles.^{11,12} The remaining gel phase, after this precipitation, is always in the hexagonal LC phase if the water content of the mixture is kept constant. Note also that the evaporation of the water component from the LC mixture promotes the crystallization of the $\text{Ag}(\text{C}_{12}\text{EO}_{10})_x\text{NO}_3$ complex.^{11,12} The samples collected from the precipitate and thick films formed at the air–LC interface of the aged samples show characteristic IR spectral features and powder X-ray diffraction (PXRD) patterns.^{11,12} The PXRD pattern of the solid-crystalline $\text{Ag}(\text{C}_{12}\text{EO}_{10})_x\text{NO}_3$ complex displays broad lines at both low- and high-angle regions of the diffraction patterns (not shown), indicating that the particles consist of small aggregates of the complex crystallites.¹²

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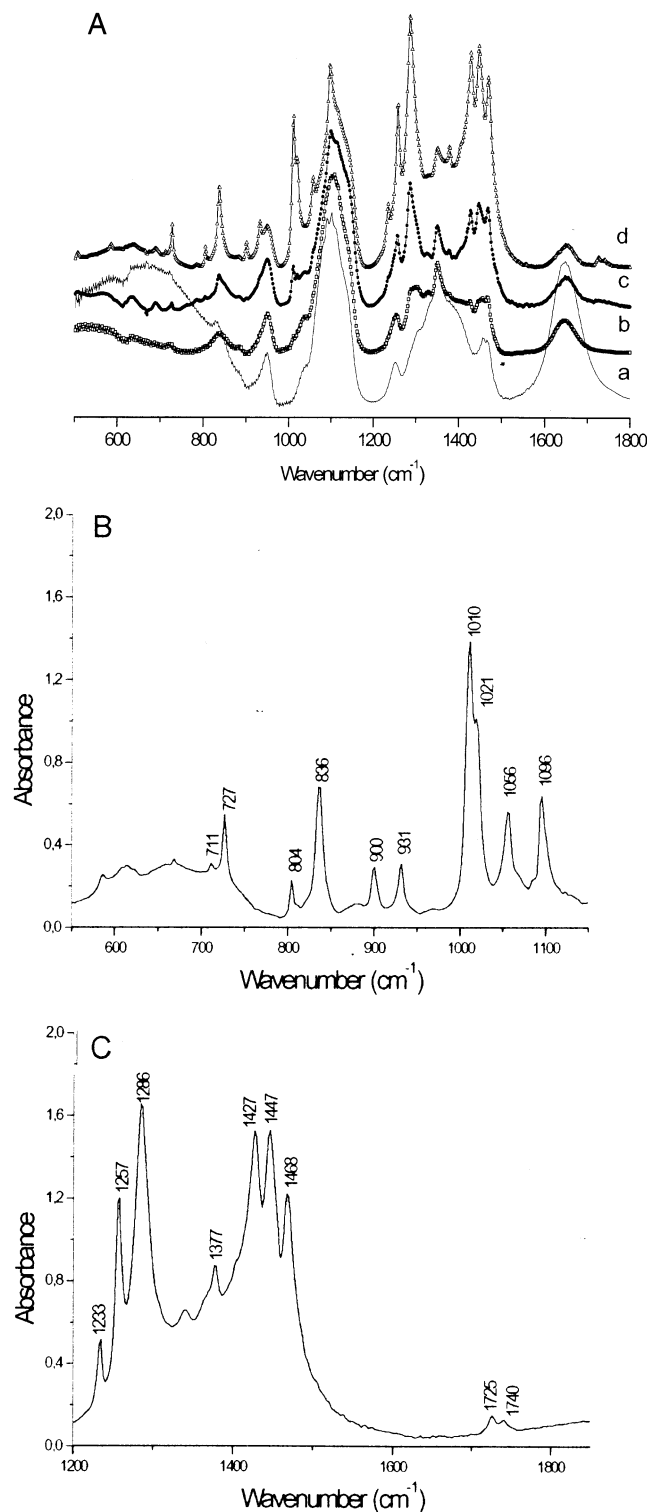


Figure 2. FTIR spectra of a system with a 0.9 mole ratio of AgNO₃ in 50% (w/w) C₁₂EO₁₀/H₂O. (A) Spectral changes during the water evaporation (a–d). Parts B and C are different regions of the same spectrum obtained from subtraction of spectral line c from d in part A.

The sharp peaks observed at 1233, 1257, 1286, 1377, 1427, 1447, and 1468 cm⁻¹ in the FTIR spectrum of the solid sample are due to the CH₂ deformation modes of C₁₂EO₁₀ and asymmetric stretching modes of the coordinated NO₃⁻ ions of the crystalline Ag(C₁₂EO₁₀)_xNO₃ complex^{11,12} (Figure 2A). Parts B and C of Figure 2 show the subtraction spectrum obtained from the two spectra recorded during the water evaporation process of the LC

phase of the AgNO₃/H₂O/C₁₂EO₁₀ system. A very small amount of AgNO₃ salt crystals and free NO₃⁻ ions present in the samples also display a sharp peak at around 1377 cm⁻¹ and a broad peak at around 1360 cm⁻¹, respectively, corresponding to the doubly degenerate asymmetric stretching modes of nitrate (Figure 2A). The difference spectrum consists of sharp peaks in the mid-IR region of the electromagnetic spectrum. Because the unidentate or bidentate coordination of the NO₃⁻ ion to a metal center lifts the symmetry, the doubly degenerate asymmetric stretching mode (E') of the NO₃⁻ ion splits into two IR-active modes. Furthermore, the Ag⁺ ion in the crystalline complex also interacts with the surfactant EO groups, giving sharper and more intense peaks in the FTIR spectrum. The sharp peaks at 1021, 1056, and 1096 cm⁻¹, most likely originating from the C–O stretching modes of the EO groups coordinated to the Ag⁺ ion, are red-shifted from the major unresolved broad band covering the 1050–1150-cm⁻¹ region. The other sharp peaks observed at 900 and 933 cm⁻¹ are also assigned to the C–O stretching mode, mixed with CH₂ rocking vibrations¹⁶ of the surfactant molecules, and reflect the local conformation changes of the EO units upon complexation.¹⁷

The interaction of the Ag⁺ ion with the EO units of the surfactant molecule is further explored using AgBF₄ and AgCF₃SO₃ salts in their ternary systems. The trend in polyelectrolyte systems is that the BF₄⁻ ions have the least binding capability and the nitrate ion has the most binding capability.^{18,19} Figure 3 shows the spectra of AgBF₄ and AgCF₃SO₃ in water-evaporated salt/water/surfactant systems and the Ag(C₁₂EO₁₀)_xNO₃-complex solid phase for the purpose of comparison. It is evident from the spectra of these systems (AgX/H₂O/C₁₂EO₁₀, where X is NO₃⁻, BF₄⁻, or CF₃SO₃⁻) that only the AgNO₃ system undergoes complex formation and phase separation. Note that the spectra of the surfactant molecules in the pure phase and water-evaporated salt/water/surfactant systems of AgBF₄ and AgCF₃SO₃ are very similar in the regions where the counteranions do not absorb. Therefore, neither the Ag⁺ cation nor the counteranion (BF₄⁻ or CF₃SO₃⁻) in these systems strongly interacts with the surfactant molecules or with each other. It has been well-established^{16,17} that the free CF₃SO₃⁻ ion absorbs at 1030 cm⁻¹, as is the case in our samples (see Figure 3). However, the same regions in the Ag(C₁₂EO₁₀)_xNO₃ crystallites consist of extra, relatively sharp peaks at 900, 933, 1021, 1056, 1096, 1233, 1257, 1427, and 1468 cm⁻¹, which originate from the coordinated surfactant molecules. The combined information from those three silver salt systems supports the idea that the nitrate ion coordinates with the Ag⁺ center, which promotes the coordination of the EO units of the surfactant molecules to the Ag⁺ ion and results in the crystallization of the Ag(C₁₂EO₁₀)_xNO₃ complex. The interactions of the nitrate ion and EO units of the surfactant molecule with the Ag⁺ ion are shown schematically in Figure 4a.

To further explore the interactions of the nitrate ions with the metal centers, the LC systems of some transition-metal nitrates {[M(H₂O)₆](NO₃)₂ and [M'(H₂O)₄](NO₃)₂, where M is Co²⁺, Ni²⁺, or Zn²⁺ and M' is Mn²⁺ or Cd²⁺} and C₁₂EO₁₀ have also been studied.¹³ In the new systems, the metal salts were dissolved in C₁₂EO₁₀ and homogenized as described in the literature.¹³ The hydrogen-bonding

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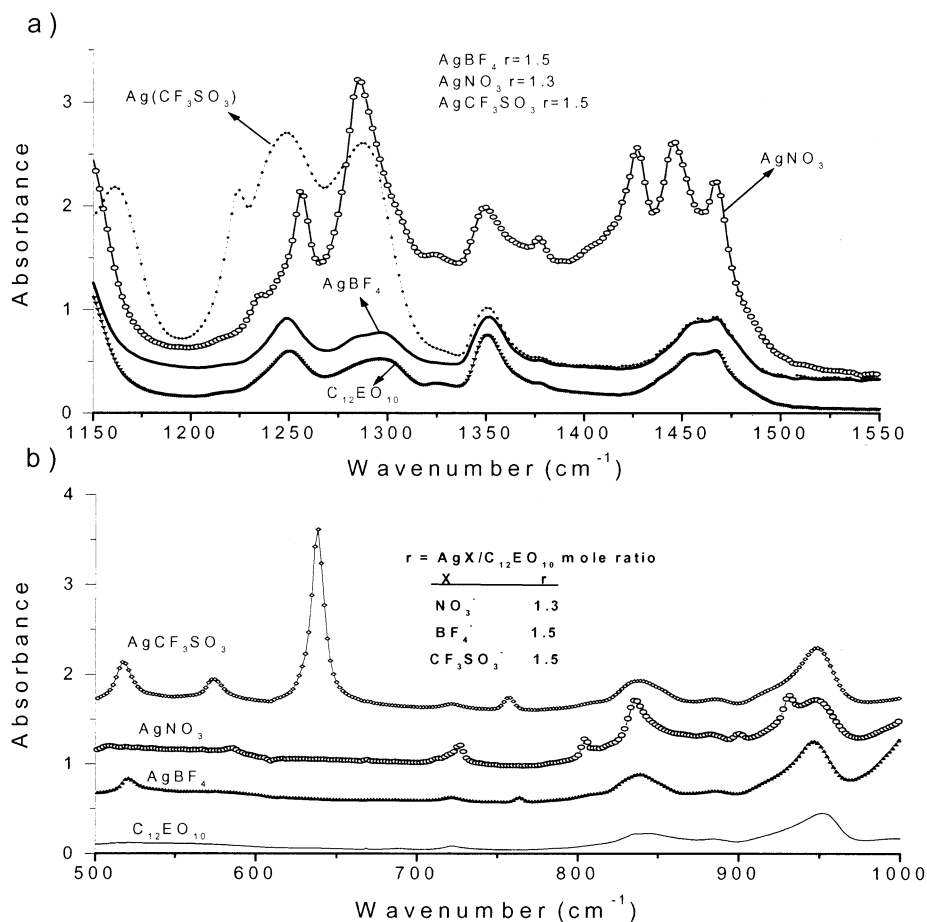


Figure 3. FTIR spectra of a AgX/H₂O/C₁₂EO₁₀ (where X is NO₃⁻, BF₄⁻, or CF₃SO₃⁻) mixture upon water evaporation and pure C₁₂EO₁₀ (*r* is the AgX/C₁₂EO₁₀ mole ratio).

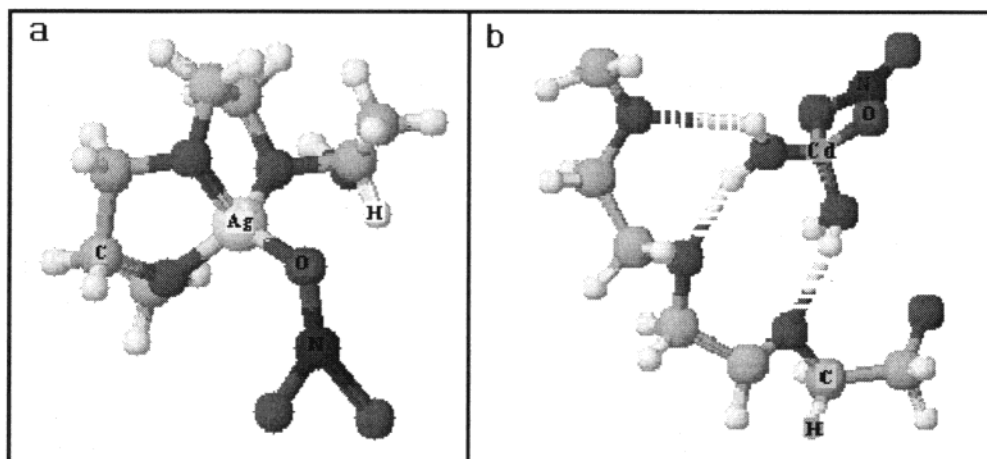


Figure 4. Schematic illustration of (a) the Ag⁺ ion interaction with the nitrate ion and surfactant molecule in the solid Ag(C₁₂EO₁₀)_xNO₃ complex and (b) the similar interaction of the [Cd(H₂O)₂(O₂NO)]⁺ cation in the LC phase of the [Cd(H₂O)₂(O₂NO)]-NO₃/C₁₂EO₁₀ system.

interaction of the coordinated water induces self-assembly in the C_{*n*}EO_{*m*}-type nonionic surfactants to give an LC mesophase.¹³

In the salt/surfactant LC systems, the nitrate ions also coordinate with the metal centers to produce [M-(H₂O)_{*n-x*}(NO₃)_{*x*}]⁺NO₃⁻ complex species in the hydrophilic domains of the LC phase. The FTIR spectra of a series of [Cd(H₂O)₄](NO₃)₂ samples (not shown) display two peaks with increasing intensity at around 1295 and 1470 cm⁻¹, corresponding to the asymmetric stretching mode of a coordinated nitrate ion (Figure 5b). Note that the splitting energy (175 cm⁻¹) corresponds to a bidentate coordina-

tion.¹⁵ The doubly degenerate in-plane bending mode of the free NO₃⁻ ion also splits into two modes upon coordination and is observed at 704 and 745 cm⁻¹. The bidentate interaction of the nitrate ion with the Cd²⁺ center is also evident from the combination bands ($\nu_1 + \nu_4$) of the nitrate ion. The peaks observed at 1727 and 1768 cm⁻¹ due to the combination modes with a spacing of 41 cm⁻¹ provide strong evidence that the nitrate ion coordinates to the metal ion as a bidentate ligand. The spectral features related to the free and coordinated nitrate ion are shown in Table 1. Inspection of the FTIR spectral changes with increasing metal-ion/surfactant mole ratio shows that

Table 1. Frequency (cm⁻¹) and Assignments of the FTIR Bands of the Nitrate Ions Coordinated to Metal Centers in the Ag(C₁₂EO₁₀)_xNO₃-Complex Crystal and [M(H₂O)_n](NO₃)₂/C₁₂EO₁₀^a Systems

assignments	Mn	Co	Ni	Ag	Cd	Zn
δ(in-plane bending, ν ₄)	<i>b</i> , 744	722, 752	<i>b</i> , 758	711, 727	704, 745	<i>b</i> , 752
δ(out-of-plane bending, ν ₂)	817	810	810, 817	804	816	813
symmetric stretching (ν ₁)	1032	1025	<i>b</i>	1010	1027	1022
asymmetric stretching (ν ₃)	1313, 1460	1300, 1480	1308, 1432	<i>c</i> , <i>c</i>	1295, 1470	1297, 1485
combination band (ν ₁ + ν ₄)	1732, 1773	1755 ^d	1760 ^d	1725, 1740	1727, 1768	1750 ^d

^a M is Mn(II), Co(II), Ni(II), Cd(II), and Zn(II). ^b Unresolved or too weak to observe. ^c Overlapped. ^d Unresolved shoulder.

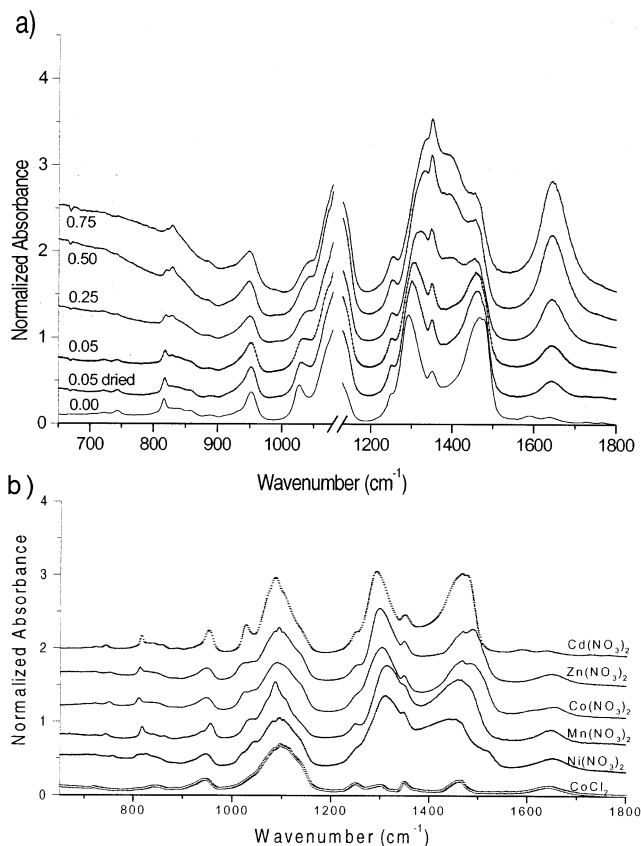
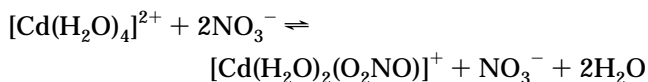


Figure 5. (a) FTIR spectral changes with varying free-water content of the 0.74:*x*:1.00 g [Cd(H₂O)₄](NO₃)₂/H₂O/C₁₂EO₁₀ systems (*x* values are listed on each spectrum). (b) FTIR spectra of the LC systems of the [Cd(H₂O)₄](NO₃)₂, [Zn(H₂O)₆](NO₃)₂, [Co(H₂O)₆](NO₃)₂, [Mn(H₂O)₄](NO₃)₂, [Ni(H₂O)₆](NO₃)₂, and [Co(H₂O)₆]Cl₂ salts and C₁₂EO₁₀ with a salt/surfactant mole ratio of 2.0.

there are no alterations of the line shape (not shown) and intensity ratios of the peaks originating from the coordinated nitrate ion, which proves the following proposed equilibrium reaction.



Variation of the water content of the mesophase confirmed the equilibrium reaction. In this context, five different samples with various water contents that did not include the coordinated water molecules {0.74 g of [Cd(H₂O)₄](NO₃)₂ dissolved in 0.00, 0.05, 0.25, 0.50, and 0.75 g of H₂O and 1.00 g of C₁₂EO₁₀} were prepared. Figure 5 shows the spectral changes observed with decreasing the amount of free water in the mixtures, which have a 1.5 Cd²⁺/C₁₂EO₁₀ mole ratio and various percentages of H₂O/C₁₂EO₁₀. The FTIR spectra of the two samples with 0.50 and 0.75 g of free water display very broad peaks at around 1360 cm⁻¹, corresponding to the free nitrate ion

dissolved in the hydrophilic region of the water/surfactant mixture. Upon a decrease in the free-water content in the [Cd(H₂O)₄](NO₃)₂/H₂O/C₁₂EO₁₀ system, the broad feature at 1360 cm⁻¹ loses its intensity while the two peaks on each side begin to emerge and dominate in this region. Note also that these two peaks due to the coordinated nitrate ions appear at around 1310 and 1450 cm⁻¹ and shift to 1295 and 1470 cm⁻¹ upon a decrease in the free-water content of the mixtures. Another important feature is the IR-inactive symmetric stretching mode of the free nitrate ion, which becomes active and is observed at around 1027 cm⁻¹. The spectrum, obtained from the dried sample, closely resembles the spectrum of the LC phase of the 1.5 mole ratio [Cd(H₂O)₄](NO₃)₂/C₁₂EO₁₀ system (bottom spectrum in Figure 5a). The nitrate ion out-of-plane bending mode also senses the changes in the varying water content. The peak at around 829 cm⁻¹ due to free nitrate loses its intensity while the shoulder at around 820 cm⁻¹ becomes intense and shifts to 816 cm⁻¹ upon a decrease in the free-water content in the mixtures. It is clear from both regions, the asymmetric stretching and in-plane bending modes, that at high water content the nitrate ions are free, undergo unidentate coordination, and then change to bidentate coordination as the water content decreases in the ternary mixtures. Notice also that the FTIR spectrum of the salt/surfactant system displays peaks at both 816 and 829 cm⁻¹ due to bidentate and free nitrate ions, which coexist in the system, proving that only one of the nitrate ions is coordinated to the cadmium center. The same FTIR spectral changes were observed for a sample prepared by dissolving 0.74 g of [Cd(H₂O)₄](NO₃)₂ in 1.00 g of H₂O and 1.00 g of C₁₂EO₁₀ (not shown) with the evaporation of its free-water content.

The spectra of the other transition-metal binary systems are very similar to that of the cadmium system (Figure 5b). The splitting energy of the asymmetric stretching of the coordinated nitrate ion in the [Mn(H₂O)₄(O₂NO)]⁺, [Co(H₂O)₄(O₂NO)]⁺, and [Zn(H₂O)₄(O₂NO)]⁺ complexes is at around 160–190 cm⁻¹, as in the cadmium case; therefore, it is likely that the bidentate coordination also dominates in these metal systems. However, the splitting energy of the asymmetric stretching modes is relatively smaller in the [Ni(H₂O)₆](NO₃)₂/C₁₂EO₁₀ system (112 cm⁻¹) and resembles a rather unidentate coordination of the nitrate ion to the Ni²⁺ center (Figure 5b). This is also evident in the out-of-plane bending mode of the nickel systems that display three distinct peaks at 825, 817, and 809 cm⁻¹, corresponding to free, unidentate-coordinated, and bidentate-coordinated nitrate ions, respectively. Each of the samples absorbs at around 825 cm⁻¹, indicating the presence of the free nitrate ion (Figure 5b). Therefore, each of the systems contain free nitrate ions and bidentate- or unidentate-type-coordinated nitrate complexes in the salt/surfactant LC phases.

The coordination of the nitrate ion to a metal center lowers the charge on the metal complex and, as a result, decreases the ionic strength of the LC phase and increases the solubilities of the salts in the C_nEO_m-type nonionic surfactants. There is an equilibrium that takes place

between the aqua complexes, $[M(H_2O)_6]^{2+}$, and the nitrated aqua complexes, $[M(H_2O)_4(O_2NO)]^+$, in the salt/surfactant systems (Figure 4b). It is possible to change the equilibrium conditions by adding extra water to these systems (Figure 5b).

In addition, we also studied the perchlorate, acetate, and iodate salts of these metal ions in the salt/surfactant systems. The detailed mesophase characterization and properties of these phases will be published elsewhere. It was discovered that the transition-metal nitrates have a high solubility in nonionic surfactants, chlorites are almost insoluble, and perchlorates are intermediately soluble. The importance of the metal–nitrate coordination is that it reduces the 2+ charge on the metal aqua complexes and ion densities of the mixtures; as a result, the crystallization of the metal salts is reduced. The only system that works in the cases of chlorites is that of $[Co(H_2O)_6]Cl_2$, which undergoes a ligand exchange reaction upon dissolution in the oligo(ethylene oxide)-type nonionic surfactants to produce $CoCl_4^{2-}$ ions and, most likely, intermediate complexes with a lower charge on the complex ions.

Conclusion

The metal complexes of the type $[M(H_2O)_n]X_2$ induce the nonionic surfactant molecules to undergo self-assembly into a LC phase. In this process, we found that the counteranion is extremely important and determines the solubility of the salt in nonionic surfactants. To explore

these findings, FTIR spectroscopy was used extensively on the samples with various metal salts in the salt/surfactant and salt/water/surfactant systems. There is a fundamental question in the literature regarding the effect of the ion–ion and ion–surfactant (or ion–polymer, ion–host) interactions on the physical properties of the surfactant molecules and poly(ethylene oxide) polymers. In this work, we have demonstrated that the nitrate ion coordinates as either a unidentate or a bidentate ligand to the metal center and decreases the ionic strength and number of ions in the salt/surfactant systems. At high ionic strengths and charge densities, the salt/surfactant systems undergo phase separation or the crystallization of the salts over time. The coordinated water molecules are very important in obtaining stable LC phases in the salt/surfactant systems. Because Ag^+ does not have a stable hydration sphere, it undergoes coordination with the EO groups of the surfactant molecules upon the evaporation of the water molecules in the medium to produce a solid-crystalline $Ag(C_{12}EO_{10})_xNO_3$ complex.

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