Inorg. Chem. **1994**, *33*, 2000–2003

Luminescence Spectroscopy of Europium(III) Nitrate, Chloride, and Perchlorate in Mixed Ethanol–Water Solutions

M. J. Lochhead,[†] P. R. Wamsley,[‡] and K. L. Bray[*,§]

Department of Chemical Engineering, Department of Physics, and Materials Science Program,
University of Wisconsin, Madison, Wisconsin 53706

Received July 8, 1993[●]

A detailed study of the luminescence properties of europium(III) nitrate, chloride, and perchlorate in mixed ethanol–water solutions has been performed. Eu^{3+} ion concentrations were varied from 0.05 to 0.5 M, and solutions ranging from aqueous to those with an ethanol/water molar ratio of 57 were investigated. Luminescence spectra and lifetimes have been used to identify inner-sphere interactions between Eu^{3+} and the counterion of the salt in solution. The frequency of the $^5D_0 \rightarrow {}^7F_0$ transition was used to identify different inner-sphere complexes. Europium nitrate complexes in the ethanol–water solutions containing one, two, and three inner-sphere nitrate ions have been observed. Lifetimes of the europium nitrate solutions ranged from 110 to 380 μs, with the longer lifetimes corresponding to solutions with a higher ethanol/water ratio and a larger number of inner-sphere nitrate ions. In the europium chloride solutions, an increased inner-sphere interaction of the chloride ion was observed as the ethanol/water ratio was increased. Lifetimes of these solutions ranged from 110 to 190 μs. Studies of europium perchlorate ethanol–water solutions indicate that the perchlorate ions do not enter the inner coordination sphere. The results of this study have particular application to the optical characterization of the sol–gel process using Eu^{3+} as a luminescent probe.

Introduction

Eu^{3+} spectroscopy is a versatile technique that has been used to characterize materials ranging from inorganic glasses to systems of biological interest.[1–3] Recently, Eu^{3+} spectroscopy was used to characterize the complicated structural evolution that takes place during the gelation and densification of materials prepared by the sol–gel process.[4–6] The use of Eu^{3+} as an optical probe in solids and solutions requires an understanding of the factors affecting the optical properties of the ion. A potentially useful set of data that is not currently available is the luminescence spectra and lifetimes of europium salts in ethanol–water solutions. Spectra and lifetimes have proven useful in the study of a number of aqueous europium salt solutions,[7–15] but the techniques have not been applied in detail to alcohol–water solutions. A limited number of investigations of rare earth ion complexation in alcohol or aqueous alcohol solutions have been performed using primarily absorption techniques.[16–20] In order to address shortcomings in existing data, we have undertaken a detailed spectroscopic investigation of europium salts in ethanol–water solutions. The purpose of this investigation was to use the luminescence properties of Eu^{3+} to assess changes in the composition of the inner coordination sphere of Eu^{3+} as the ethanol/water ratio was varied. Important Eu^{3+} luminescence features used include the $^5D_0$ luminescence lifetime, the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition, and the frequency of the nondegenerate $^5D_0 \rightarrow {}^7F_0$ transition. The spectroscopic properties of the Eu^{3+} ion are discussed in more detail in the book by Bunzli and Choppin.[1]

Experimental Section

Sample Preparation. All solutions were prepared by dissolving hydrated Eu^{3+} salts in appropriate amounts of spectrophotometric grade ethanol (Aldrich) and deionized water. The ethanol to water molar ratio was varied from 0 (aqueous solution) to 57 (hydrated precursor dissolved in ethanol). Eu^{3+} precursors based on three counterions were used: Eu(NO$_3$)$_3$·6H$_2$O (Aldrich), EuCl$_3$·6H$_2$O (Aldrich), and Eu(ClO$_4$)$_3$·6H$_2$O (GFS Chemicals). The waters of hydration were included in the calculation of the ethanol/water ratio.

Spectroscopic Measurements. Continuous-Wave Luminescence. Continuous-wave luminescence spectra were obtained by using the 465.8-nm line of a Coherent Innova 70 Series argon ion laser to pump the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+}. Efficient nonradiative decay between the $^5D_2$ and $^5D_0$ states occurs in Eu^{3+}, and the luminescence spectra are dominated by transitions between the $^5D_0$ and ^7F_J states. Luminescence was collected in front-face mode and was focused on the entrance slit of a SPEX 1000M 1-m monochromator. A 515 nm long pass dielectric filter was used at the entrance slit to minimize stray laser light. The detector was a multialkali photomultiplier tube connected to photon-counting electronics and software (SPEX Auto Scan).

Time-Resolved Luminescence. Time-resolved measurements were obtained using a Spectra-Physics PDL-3 pulsed dye laser pumped with a Continuum NY-61 Q-switched Nd:YAG laser. The dye was a 1/1 mixture of rhodamine 590 and rhodamine 610 (Exciton, Inc.) and provided the tunable laser light from 570 to 592 nm used to pump the $^7F_0 \rightarrow {}^5D_0$

---

[*] Author for correspondence: Department of Chemical Engineering; phone (608) 262-9053; fax (608) 262-5434; email bray@engr.wisc.edu.

[†] Department of Chemical Engineering.

[‡] Department of Physics.

[§] Department of Chemical Engineering and Materials Science Program.

[●] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

(1) Bunzli, J.-C. G.; Choppin, G. R. *Lanthanide Probes in the Life, Chemical, and Earth Sciences*; Elsevier: New York, 1989.
(2) Yen, W. M. In *Optical Spectroscopy of Glasses*; Zschokke, I., Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1986; pp 23–64.
(3) Richardson, F. S. *Chem. Rev.* **1982**, *82*, 541.
(4) Ferrari, M.; Campostrini, R.; Carturan, G.; Montagna, M. *Philos. Mag. B* **1992**, *65*, 251.
(5) McDonagh, C.; Ennis, G.; Marron, P.; O'Kelly, B.; Tang, T. R.; McGilp, J. F. *J. Non-Cryst. Solids* **1992**, *147* and *148*, 97.
(6) Levy, D.; Reisfeld, R.; Avnir, D. *Chem. Phys. Lett.* **1984**, *109*, 593.
(7) Albin, M.; Horrocks, W. DeW., Jr. *Inorg. Chem.* **1985**, *24*, 895.
(8) Breen, P. J.; Horrocks, W. DeW., Jr. *Inorg. Chem.* **1983**, *22*, 536.
(9) Bunzli, J.-C. G.; Yersin, J.-R. *Inorg. Chem.* **1979**, *18*, 605.
(10) Piriou, B.; Svoronos, D.-R. *J. Less-Common Met.* **1985**, *112*, 275.
(11) Tanaka, F.; Yamashita, S. *Inorg. Chem.* **1984**, *23*, 2044.
(12) Lis, S.; Choppin, G. R. *Mater. Chem. Phys.* **1992**, *31*, 159.
(13) Horrocks, W. DeW., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334.
(14) Kropp, J. L.; Windsor, M. W. *J. Chem. Phys.* **1965**, *42*, 1599.
(15) Silber, H. B.; Bakhshandefar, R.; Contreras, L. A.; Gaizer, F.; Gonsalves, M.; Ismail, S. *Inorg. Chem.* **1990**, *29*, 4473.
(16) Silber, H. B.; Strozier, M. S. *Inorg. Chim. Acta* **1987**, *128*, 267.
(17) Hamze, M.; Meullemeestre, J.; Schwing, M. J.; Vierling, F. *J. Less-Common Met.* **1986**, *118*, 153.
(18) Haas, Y.; Stein, G. *J. Phys. Chem.* **1971**, *75*, 3668.
(19) Abrahamer, I.; Marcus, Y. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1563.
(20) Dawson, W. R.; Kropp, J. L. *J. Opt. Soc. Am.* **1965**, *55*, 822.

0020-1669/94/1333-2000$04.50/0

Table 1. Europium Salt Ethanol–Water Solution Lifetimes[a]

europium nitrate			europium chloride		
$[Eu^{3+}]$, mol/L	molar ratio EtOH/H_2O	lifetime ±5 μs	$[Eu^{3+}]$, mol/L	molar ratio, EtOH/H_2O	lifetime, ±5 μs
0.05	57	380			
0.1	1	157	0.1	1	112
	2	179		2	123
	3	196		3	129
	4	200		4	133
	5	225		5	134
	28	380		28	190
0.3	1	157	0.3	1	125
	2	198		2	137
	3	222		3	137
	4	250		4	135
	5	261		5	138
	9.5	315		9.5	179
0.5	1	175	0.5	1	118
	2	215		2	123
	3	250		3	143
	4	262		4	146
	5.7	280		5.7	162

[a] Anion concentration is 3 times the Eu^{3+} concentration in all solutions. Excitation is at the maximum of the $^7F_0 \rightarrow {}^5D_0$ absorption band. $^5D_0$ luminescence was monitored at 617 nm for the nitrate solutions and 698 nm for the chloride solutions.

and $^7F_1 \rightarrow {}^5D_0$ transitions. The laser pulses were approximately 9 ns in duration at a 10-Hz repetition rate, with a bandwidth of ≤1 cm^{-1}.

Front-face fluorescence was collected and focused on the entrance slit of a SPEX 1704 1-m monochromator. A 600 nm long pass dielectric filter was used at the entrance slit of the monochromator to minimize stray laser light. When fluorescence lifetimes were measured, the monochromator was set to the strongest, low-noise luminescence band of a given sample. This was normally the $^5D_0 \rightarrow {}^7F_2$ transition near 617 nm or the $^5D_0 \rightarrow {}^7F_4$ transition near 698 nm.

The luminescence was detected with a Hamamatsu R2228 photomultiplier tube. The signal from the tube was sent to the input port of a Stanford Research Systems SR250 gated boxcar integrator. An electronic pulse synchronized to the YAG laser Q-switch was used to trigger the electronics. Luminescence decay was measured by scanning the delay of a sampling gate in time, using software developed by Stanford Research Systems (SR270). In order to minimize random noise and the effects of shot-to-shot variation of the laser pulses, at least 20 scans were averaged when fluorescence decay spectra were generated. Lifetimes were determined from best fit exponentials of the decay curves.

The time-resolved system was also used to generate excitation spectra of the $^7F_0 \rightarrow {}^5D_0$ transition. Excitation spectra were measured by scanning the dye laser across the $^7F_0 \rightarrow {}^5D_0$ transition while the strongest fluorescence band was detected in photon-counting mode.

Results and Discussion

Europium Nitrate Ethanol–Water Solutions. Room-temperature luminescence lifetimes of the $^5D_0$ state are presented in Table 1. For a fixed Eu^{3+} concentration ($[NO_3^-] = 3[Eu^{3+}]$), we observe a dramatic lengthening of the lifetime as the ethanol/water molar ratio is increased. All of the ethanol/water solution lifetimes are significantly longer than those observed in aqueous europium nitrate solutions.[9,11,12] We attribute this result to an increased inner-sphere interaction between NO_3^- and Eu^{3+} as the ethanol/water ratio is increased. As the ethanol/water ratio is increased, the ability of water to compete for position in the inner coordination sphere of Eu^{3+} decreases. As a consequence, the increased probability of observing inner-sphere NO_3^- ions leads to a less-effective nonradiative deexcitation of the $^5D_0$ state.[13] Our interpretation is consistent with absorption studies,[16,19,20] which demonstrate the ability of NO_3^- to coordinate to Eu^{3+} in alcoholic solutions. A similar lifetime trend is observed as the $Eu(NO_3)_3 \cdot 6H_2O$ concentration is increased for a fixed ethanol/water ratio.

Our argument assumes that the possibility of increased coordination of ethanol to Eu^{3+} as the ethanol/water ratio is increased is unimportant. This assumption is consistent with work performed by Abrahamer and Marcus,[19] which shows that water and NO_3^- have comparable abilities to coordinate to Eu^{3+} and that ethanol coordinates to Eu^{3+} much more weakly than either water or NO_3^-. We expect ethanol to have a significant effect on the luminescence properties of Eu^{3+} only for extremely high ethanol/water ratios. We provide further support for this assumption in our studies of the perchlorate solutions discussed below.

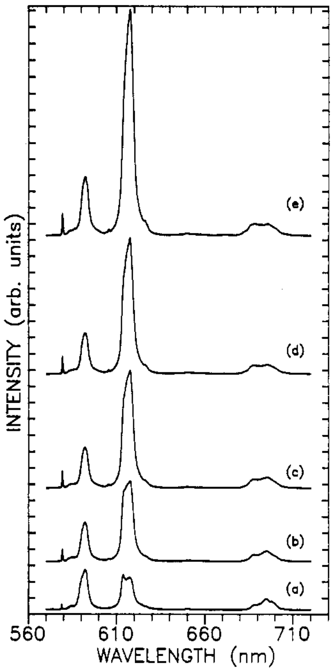

Figure 1. Room-temperature luminescence spectra of europium nitrate solutions as a function of ethanol/water molar ratio (λ_{ex} = 465.8 nm, $[Eu^{3+}]$ = 0.5 M, $[NO_3^-]$ = 1.5 M): (a) aqueous solution; (b) ethanol/water = 1; (c) ethanol/water = 2; (d) ethanol/water = 3; (e) ethanol/water = 5.7. All spectra are normalized to the $^5D_0 \rightarrow {}^7F_1$ transition at 592.5 nm.

Further consequences of an increased inner-sphere interaction between NO_3^- and Eu^{3+} are seen in Figure 1, which illustrates luminescence spectra of 0.5 M $Eu(NO_3)_3 \cdot 6H_2O$ solutions as the ethanol/water ratio is increased from 0 (aqueous solution) to 5.7. Here we see a significant increase in the relative intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition (617 nm) as the ethanol/water ratio is increased. In addition, the forbidden $^5D_0 \rightarrow {}^7F_0$ (579 nm) transition gains relative intensity as the ratio is increased. These intensity increases are consistent with the removal of inversion symmetry that accompanies inner-sphere coordination of NO_3^-.[21]

A more detailed understanding of the nature of NO_3^- coordination to Eu^{3+} is obtained by examining high-resolution $^5D_0 \rightarrow {}^7F_0$ luminescence spectra. We measured both $^5D_0 \rightarrow {}^7F_0$ luminescence and $^7F_0 \rightarrow {}^5D_0$ excitation spectra (monitoring luminescence at 617 nm). Both techniques yielded similar results. The signal to noise ratio was superior in the luminescence spectra, so these results are presented in Figure 2. In addition to the $Eu(NO_3)_3 \cdot 6H_2O$ solution spectra, the $^5D_0 \rightarrow {}^7F_0$ luminescence spectrum of an aqueous $Eu(ClO_4)_3 \cdot 6H_2O$ solution is included for comparison (Figure 2a) and will be discussed shortly.

Breen and Horrocks[8] and Albin and Horrocks[7] have discussed a nephelauxetic effect in which the $^7F_0 \rightarrow {}^5D_0$ transition shifts to lower frequency as the combined charge of all ligands coordinated to Eu^{3+} becomes more negative. We have used the data presented in the development of that correlation[7] to assign distinct europium nitrate complexes to the peaks observed in our

---

(21) Peacock, R. D. *Struct. Bonding* **1975**, *22*, 83.

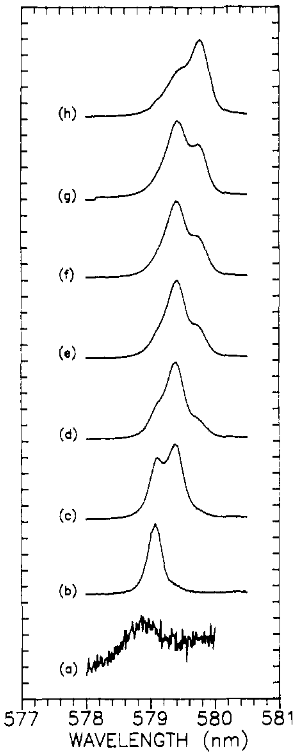

Figure 2. Room-temperature luminescence spectra of the $^5D_0 \rightarrow {}^7F_0$ transition in europium nitrate solutions as a function of ethanol/water molar ratio (λ_{ex} = 465.8 nm): (a) aqueous europium perchlorate solution, [Eu^{3+}] = 1.0 M; (b) aqueous europium nitrate solution, [Eu^{3+}] = 0.5 M; (c) europium nitrate, [Eu^{3+}] = 0.5 M, ethanol/water = 1; (d) europium nitrate, [Eu^{3+}] = 0.5 M, ethanol/water = 2; (e) europium nitrate, [Eu^{3+}] = 0.5 M, ethanol/water = 3; (f) europium nitrate, [Eu^{3+}] = 0.5 M, ethanol/water = 4; (g) europium nitrate, [Eu^{3+}] = 0.5 M, ethanol/water = 5.7; (h) europium nitrate, [Eu^{3+}] = 0.05 M, ethanol/water = 57. Spectra are normalized to the $^5D_0 \rightarrow {}^7F_0$ peak intensity.

$^5D_0 \rightarrow {}^7F_0$ luminescence spectra. We did not fit the peaks of Figure 2 to determine the transition frequencies. Instead, we estimated the peak positions directly from the spectra. We believe the four peaks readily discernible in Figure 2 are sufficiently resolved to allow peak determination to within a few cm^{-1}, which is within the scatter in the data used to develop the Albin and Horrocks correlation.

Figure 2a shows the relatively weak $^7F_0 \rightarrow {}^5D_0$ excitation spectrum for the $Eu(ClO_4)_3{\cdot}6H_2O$ aqueous solution. The perchlorate ion does not enter the inner coordination sphere of Eu^{3+} in aqueous solutions of this salt concentration,[9,11,12] so the peak shown in Figure 2a (centered near 578.9 nm (17 274 cm^{-1})) corresponds to the fully hydrated aquo ion of Eu^{3+}.[7]

The remaining spectra in Figure 2 correspond to $Eu(NO_3)_3{\cdot}6H_2O$ solutions with increasing ethanol/water ratios. Three distinct peaks are clearly observed as the ethanol/water ratio is varied. In the aqueous $Eu(NO_3)_3{\cdot}6H_2O$ solution (Figure 2b), the luminescence is dominated by a single, sharp feature centered near 579.1 nm. For the most ethanol-rich solution (Figure 2h), the dominant feature is a sharp peak centered near 579.7 nm. At the intermediate ethanol/water ratios, a peak centered at 579.4 nm dominates. The relative intensities of the three peaks increase and decrease continuously as the ethanol/water ratio is varied. The presence of three peaks suggests the presence of three distinct europium nitrate complexes in ethanol–water solutions.

The peak at 579.1 nm (17 268 cm^{-1}) has been attributed to an aqueous europium complex containing one inner-sphere NO_3^-.[8] In the $Eu(NO_3)_3{\cdot}6H_2O$ solution with an ethanol/water molar ratio of 1 (Figure 2c), we continue to observe the peak at 579.1 nm, but we seen an even stronger peak near 579.4 nm (17 259 cm^{-1}). We attribute this new peak to an Eu^{3+} complex containing two inner-sphere NO_3^- ions. The assignment is consistent with the literature value of the peak energy (17 261 cm^{-1}) for the $[Eu(NO_3)_2(H_2O)_x]^+$ complex.[8] As the ethanol/water ratio is increased further, the peak at 579.1 nm loses intensity while a low-energy shoulder develops and gains intensity (Figure 2d–g). This shoulder becomes the dominant peak in Figure 2h and is centered near 579.7 nm (17 250 cm^{-1}). Assuming a continuous trend in Eu^{3+} complexation, we attribute this peak to a complex containing three inner-sphere nitrate ions. We believe the spectra presented in Figure 2 and our assignment of peaks to europium nitrate complexes containing one, two, and three inner-sphere nitrate ions corroborate the correlation developed by Albin and Horrocks.[7]

Our assignment of the peak at 579.7 nm to a tris(nitrato)europium complex must be considered in light of the fact that we (and others) have measured a $^5D_0 \rightarrow {}^7F_0$ transition at 579.3 nm for the solid $Eu(NO_3)_3{\cdot}6H_2O$ complex.[7] We believe the wavelength discrepancy results from structure and bonding differences between solid-state and solution complexes. During development of their correlation, Albin and Horrocks[7] note that for compounds with a combined ligand charge of −3, the data showed the least agreement between solids and solutions. Given this observation and the continuous trends observed in our lifetime and spectral data, we believe we have correctly assigned the 579.7-nm peak in our solutions.

Europium Chloride Ethanol–Water Solutions. Room-temperature luminescence lifetime data for the europium chloride ethanol–water solutions are provided in Table 1. As was observed in the europium nitrate solutions, we see lengthening of the luminescence lifetimes as the ethanol/water ratio is increased. Note, however, that this effect is much less significant in the chloride solutions. This suggests that Cl^- ions have a lower affinity for the Eu^{3+} inner coordination sphere in ethanol–water solutions than do NO_3^- ions. The fact that the lifetimes are longer in the ethanol–water solutions than they are in the aqueous solutions (~110 μs)[11] indicates that the chloride ions are more effective at entering the inner coordination sphere in the ethanol–water solutions.

Figure 3 illustrates luminescence spectra for $EuCl_3{\cdot}6H_2O$ solutions with ethanol/water ratios ranging from 0 to 5.7. Here we see the appearance and growth of a sharp feature (612 nm) in the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition and an increase in the relative intensity of the $^5D_0 \rightarrow {}^7F_0$ transition as the ethanol/water ratio is increased. Both of these results suggest a distortion of the Eu^{3+} bonding environment, which we attribute to the inner-sphere coordination of Cl^- to Eu^{3+}.

High-resolution $^5D_0 \rightarrow {}^7F_0$ luminescence spectra of these solutions consist of a single peak centered near 579.0 nm (17 271 cm^{-1}). The peak grows in intensity as the ethanol/water ratio is increased (see Figure 3), but no additional peaks or shoulders appear in the spectra. The 579.0-nm peak has been attributed to an aqueous Eu^{3+} complex containing a single, inner-sphere Cl^- ion.[8] The $^5D_0 \rightarrow {}^7F_0$ spectra indicate that no more than one Cl^- ion enters the inner coordination sphere in these solutions.

Europium Perchlorate Ethanol–Water Solutions. Luminescence lifetimes and spectra for $Eu(ClO_4)_3{\cdot}6H_2O$ solutions have been measured over the same ranges of Eu^{3+} concentrations and ethanol/water ratios used in the $Eu(NO_3)_3{\cdot}6H_2O$ and $EuCl_3{\cdot}6H_2O$ studies. We observed essentially no variation in our spectral and lifetime data for the $Eu(ClO_4)_3{\cdot}6H_2O$ solutions as we varied the ethanol/water ratio. The lifetimes and spectra consistently match the results reported for aqueous solution.[9,11,12] This indicates that there is no inner-sphere interaction between ClO_4^- ions and Eu^{3+} in our ethanol–water solutions.

The inability of ClO_4^- to coordinate to Eu^{3+} in aqueous solution has been well-documented.[9,11,12] The absence of inner-sphere ClO_4^- is significant because it means solutions of $Eu(ClO_4)_3{\cdot}6H_2O$

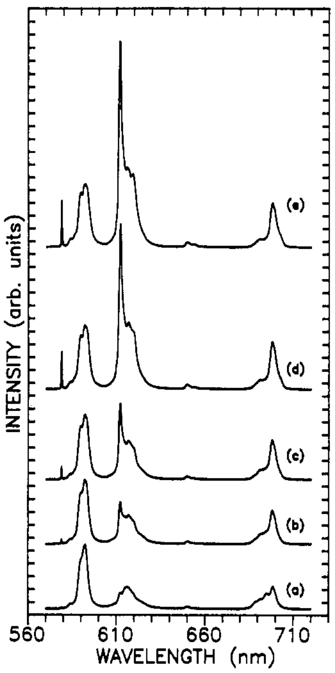

Figure 3. Room-temperature luminescence spectra of europium chloride solutions as a function of ethanol/water molar ratio (λ_{ex} = 465.8 nm, $[Eu^{3+}]$ = 0.5 M, $[Cl^-]$ = 1.5 M): (a) aqueous solution; (b) ethanol/water = 1; (c) ethanol/water = 2; (d) ethanol/water = 4; (e) ethanol/water = 5.7. All spectra are normalized to the $^5D_0 \rightarrow {}^7F_1$ transition at 592.5 nm.

can be used to assess the relative coordinating abilities of water and ethanol molecules. It is well-known that alcohol molecules are less-effective at quenching Eu^{3+} luminescence than water molecules.[19] Consequently, the replacement of water molecules with alcohol molecules in the inner coordination sphere of Eu^{3+} would lead to a lengthening of the luminescence lifetime. Since our data reveal no increase in lifetime as the ethanol/water ratio is increased, we conclude that inner-sphere coordination of ethanol is unimportant over the range of ethanol/water ratios considered. The constant measured intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition as the ethanol/water ratio is varied supports this conclusion because it reflects the absence of the geometric distortion of the inner coordination sphere that would accompany ethanol coordination.

Conclusions

We have performed a detailed study of the luminescence properties of europium nitrate, chloride, and perchlorate in ethanol–water solutions. Luminescence spectra and lifetimes were used to identify inner-sphere complexation of Eu^{3+} by the counterion of the salt. In the $Eu(NO_3)_3{\cdot}6H_2O$ solutions, increased ethanol/water ratios led to a strong inner-sphere interaction, and complexes containing one, two, and three inner-sphere nitrate ions were identified. Cl^- ions were shown to have a lower affinity for the Eu^{3+} inner coordination sphere, and evidence for only one inner-sphere Cl^- ion was obtained even for high ethanol/water ratios. Perchlorate ions did not enter the inner-coordination sphere in any of the ethanol–water solutions considered here.

We conclude with a remark on the application of these results to the investigation of the silica sol–gel process using Eu^{3+} spectroscopy. Existing studies[4–6] interpret changes in the structure of the silica matrix during gelation and densification by analyzing changes in the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition, the $^5D_0 \rightarrow {}^7F_0$ transition, and the luminescence lifetime. The results presented in our current study show that changes in these parameters are not necessarily indicative of an interaction between Eu^{3+} and the silica matrix during the early stages of the sol–gel process. Counterion complexation can play a significant role in determining luminescence properties, especially when $Eu(NO_3)_3{\cdot}6H_2O$ is used to introduce the Eu^{3+} probe ion. We will discuss the application of Eu^{3+} luminescence properties to the characterization of the sol–gel process in future work.[22]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the research. We also acknowledge partial financial support from the National Science Foundation, Division of Earth Sciences, and fellowship support from the Amoco Corp. (M.J.L.).

---

(22) Lochhead, M. J.; Bray, K. L. *J. Non-Cryst. Solids*, in press.