Spectroscopic Properties of Lanthanide (III) Compounds in Aqueous and Ionic Media

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Introduction:

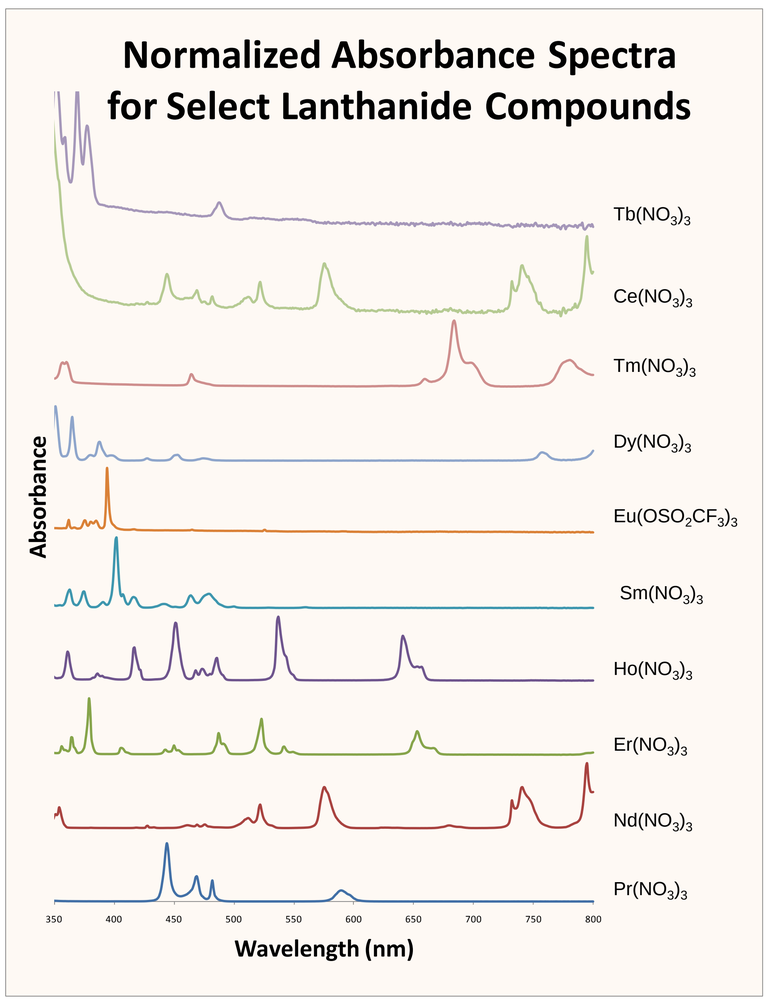
Lanthanide containing materials are receiving increasing attention due to their wide range of potential applications including bioanalytical imaging, dye-sensitized solar cells, nano-biotechnology and catalysis. The unique spectroscopic properties (intense and sharp emission bands with high color purity and high quantum efficiency) of lanthanides make them strong candidates for use as bio-markers or selective detectors. The attractiveness of lanthanides as future imaging agents as well as recent interest in their potential use in biological media has increased the need to understand the behavior of lanthanides in the presence of other ions or in ionic media.

The complexity of the biological media and the diversity and variability of the ions present in it makes it important to be aware of any interactions between the lanthanide complexes and ions. The focus of this research is to add to the knowledge base on the absorption and emission behavior of various lanthanide complexes in the presence of a range of ionic media. This study is designed towards understanding the spectroscopic behavior of lanthanides in ionic environments.

Sample Preparation:

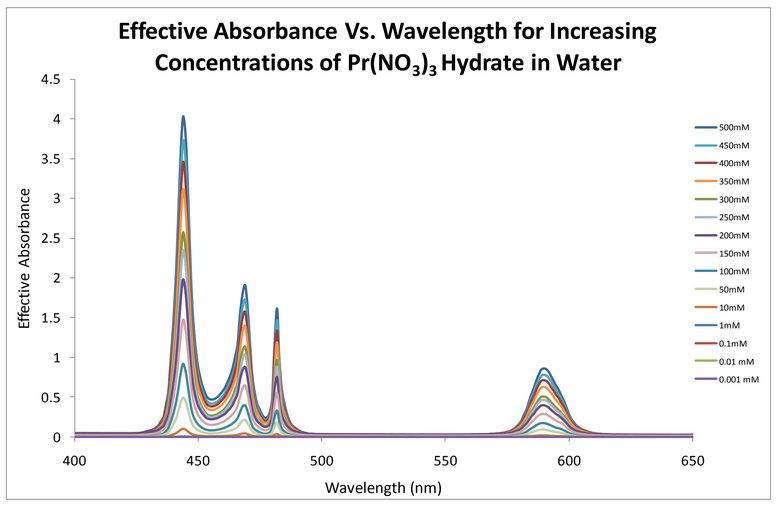
Individual samples were prepared in 20 mL scintillation vials. Each sample was individually weighed on an analytical balance and added to 10 mL of de-ionized water, NaCl, or $MgCl_2$.

UV-Visible Absorbance Results:

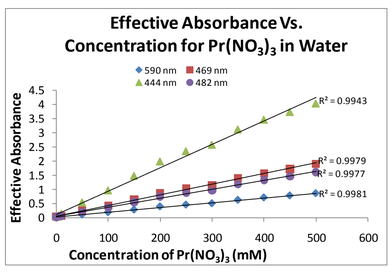


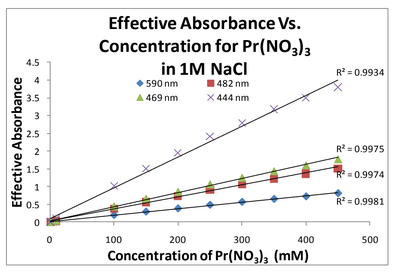
- Several lanthanide nitrates including, Ce^{4+}, La^{3+}, Lu^{3+}, Gd^{3+}, and Yb^{3+}, did not show any absorbance in the studied region.
- A large ligand peak was observed in all nitrates around the 280 - 300 nm wavelength.

Concentration Dependence of Praseodymium(III) Nitrate in water:

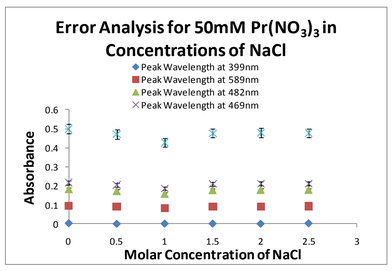


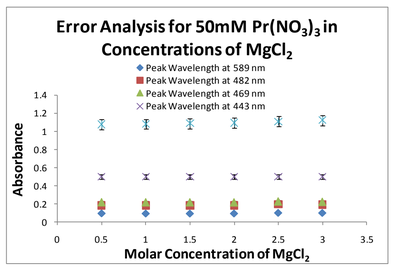
Beer-Lambert's Plots for Praseodymium (III) Nitrate:





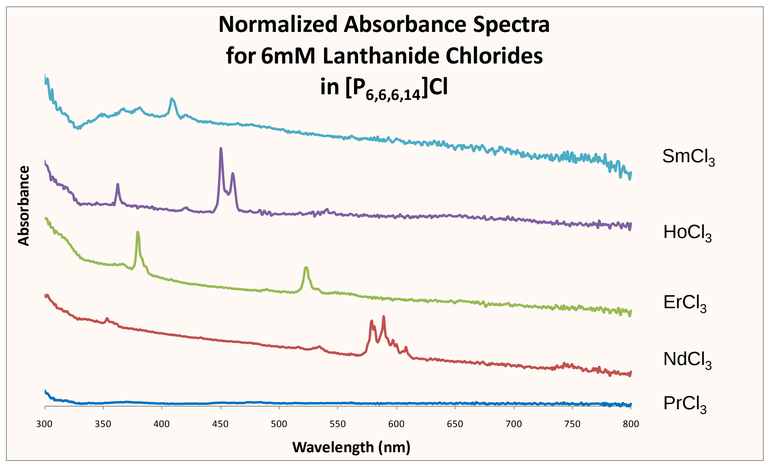
Absorbance of praseodymium (III) nitrate at different peaks was found to vary linearly with concentration, suggesting that praseodymium (III) nitrate obeys the Beer-Lambert law in water, NaCl and $MgCl_2$ solutions.





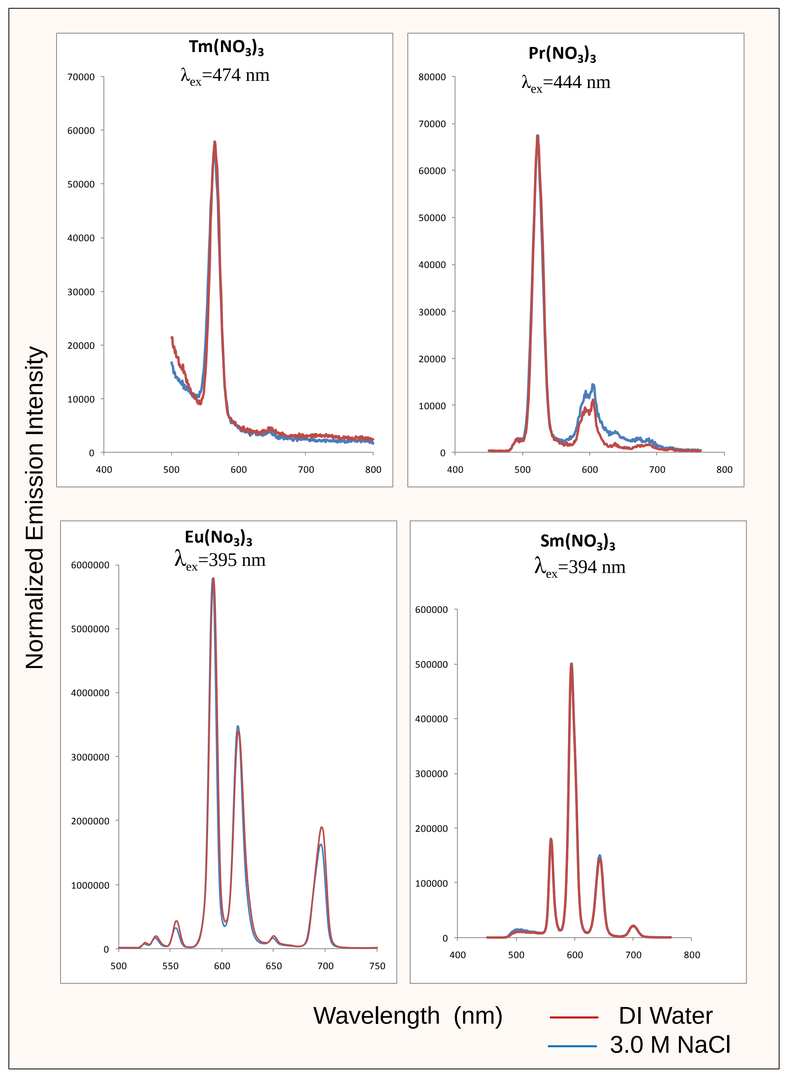
NaCl and $MgCl_2$ produced no significant changes in the absorbance intensity of praseodymium (III) nitrate.

Absorbance in Ionic Liquids:



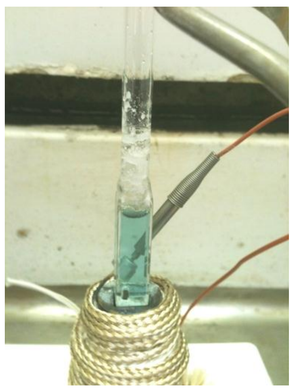
Samples of select lanthanide chlorides ($NdCl_3$, $HoCl_3$, $ErCl_3$, $PrCl_3$, $SmCl_3$, and $EuCl_3$) were prepared in 3 distinct ionic liquids (Butyl-trimethyl-ammonium-*bis*(trifluoromethylsulfonyl)imide, Trihexyltetradecylphosphonium chloride $[P_{6,6,6,14}]Cl$, and 1-butyl-methylimidazoliumtrifluoromethane sulfonate [BMIMOTF]. Lanthanide nitrates dissolved well in both the $[P_{6,6,6,14}]Cl$, and [BMIMOTF], however samples in the imide did not go into solution.

Emission Spectra for Select Lanthanide Chlorides in DI Water and 3M NaCl:



Conclusion and Future Directions:

- Praseodymium(III) Nitrate was found to obey the Beer-Lambert's Law in aqueous solution.
- While NaCl and $MgCl_2$ did not affect the absorbance spectra, NaCl did appear to slightly alter the emission spectra of lanthanide nitrates.
- The next steps would be to measure the emission of lanthanide compounds in ionic liquids and to consider lanthanide compounds in molten salts. Further consideration should also be given to lanthanide and ion interactions through a broader pH range.



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