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Tb^{3+} and Eu^{3+} luminescence in imidazolium ionic liquids

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ABSTRACT

The luminescence properties of Tb^{3+} and Eu^{3+} dissolved in ionic liquids are studied. Solutes in this study include simple lanthanide compounds (e.g., $EuBr_3$, $TbCl_3$) and lanthanide complexes (e.g., $Eu(dpa)_3{}^{3-}$ where dpa = 2,6 pyridine dicarboxylate dianion) dissolved in a 1-butyl-3-methylimidazolium bromide(BMIBr)/water mixture. Emission, excitation, and time-resolved emission measurements are utilized to characterize the spectroscopic properties. It is well established in the literature that the solubility and spectroscopic properties of lanthanides in ionic liquids are highly dependent upon environmental factors including purity, and water content [K. Binnemans, Chemical Reviews (2007); I. Billard, S. Mekki, C. Gaillard, P. Hesemann, C. Mariet, G. Moutiers, A. Labet, J.-C.G. Bünzli, European Journal of Inorganic Chemistry 6 (2004) 1190–1197; S. Samikkanu, K. Mellem, M. Berry, P.S. May, Inorganic Chemistry 46 (2007) 7121–7128]. The water in this ionic liquid system acts as a co-solvent to facilitate solubility of Tb^{3+} and Eu^{3+} compounds. The observed spectroscopic properties of Eu^{3+} and Tb^{3+} salts are expectedly impacted by the high water content, but unexpectedly impacted by the BMIBr ionic liquid. However, the spectroscopy of $Eu(dpa)_3{}^{3-}$ is unaffected by the presence of BMIBr.

1. Introduction

There have been a number of studies of the solubility, separations and luminescent properties of lanthanide and actinide compounds in ionic liquids [1,4–10]. Many of these studies use ionic liquids based upon alkylmethylimidazolium (RMI^+) cations with the anion chosen based upon its properties ((e.g., water miscibility, coordination ability) [11]. Because even the hydrophobic (immiscible with water) ionic liquids are somewhat hygroscopic [2], the purity and water content of the ionic liquid play a large role in the properties ((e.g., coordination and spectroscopic) demonstrated by the dissolved metal ions [12]. Because lanthanide ions are particularly sensitive to the presence of water [13], any effort to study lanthanide luminescence in ionic liquids must account for the role of water.

In a study by Billard, et al. [2] of a hydrophobic ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfon)imide ($BMITf_2N$), the presence of water seems to cause Eu^{3+} to dissolve within aggregates of water in the ionic liquid. However, in a water miscible ionic liquid, 1-butyl-3-methylimidazolium chloride (BMICl), the Eu^{3+} coordination environment and luminescence properties are unaffected by the presence of water up to a 1:1 water to ionic liquid mole ratio [3]. This shows that the coordinating ability of the anion is more important than water miscibility of the imidazolium ionic liquid for Eu^{3+} luminescence.

In this study, the authors report a spectroscopic study of Eu^{3+} and Tb^{3+} compounds dissolved in a 1-butyl-3-methylimidazolium bromide (BMIBr)/water mixture. The lanthanide compounds studied include some simple salts, $EuBr_3{\cdot}6H_2O$, $EuCl_3{\cdot}6H_2O$, $TbCl_3{\cdot}6H_2O$, and the complex $Eu(dpa)_3{}^{3-}$ (where dpa = 2,6-pyridinedicarboxylate). These studies were conducted in the binary solvent (BMIBr/water), where the water acts as a co-solvent to facilitate the solubility of the compounds. Excitation, emission and time-resolved emission spectroscopic measurements were used to examine the impact of this binary solvent environment on the Eu^{3+} and Tb^{3+} luminescence. Spectroscopic measurements of the simple chloride and bromide salts were conducted to provide a comparison of BMIBr/water with similar lanthanide salts dissolved in imidazolium ionic liquid systems in the literature [3,4,14]. Spectroscopic measurements of the $Eu(dpa)_3{}^{3-}$complexes were conducted to investigate the stability of these complexes in BMIBr/water, because of their potential use as probes of intermolecular interactions (particularly for chiral recognition studies) [15] in ionic liquid solvent systems.

2. Experimental

2.1. Preparation of BMIBr

The BMIBr ionic liquid was prepared by stirring equimolar mixture of methylimidazole and bromobutane under nitrogen at 70 °C for 48 h. The resulting yellow solid was washed with ethyl acetate and stored in a vacuum dessicator. It was found that

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the BMIBr solid is so hygroscopic that it picks up enough water when exposed to air to become a liquid at room temperature. Attempts to remove all of the water by degassing were unsuccessful. Therefore, the liquids were prepared by leaving some of the solid out of the dessicator for >24 h. Attempts to remove the yellow color ((e.g., mixing with carbon black, using an alumina column) yielded little change [12], and did not affect the behavior (i.e. solute solubility, or spectroscopic interference) of the ionic liquids observed in this study. All of the ionic liquid used in this study is a mixture of BMIBr and water. The water content was 5 wt.% as determined by Karl Fischer titration (MetroOhm, Titrino Plus 870) prior to addition of the lanthanide samples.

2.2. *Sample preparation*

The $EuBr_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$, and $TbCl_3 \cdot 6H_2O$ were purchased from Aldrich and used as received. The lanthanide salts were dissolved in the BMIBr/water mixture by stirring for ∼24 h. Except where otherwise stated, all sample concentrations are ca. 100×10^{-3} molal europium or terbium. In some instances samples were degassed at room temperature to increase solubility. Aqueous samples of $EuBr_3$ (10×10^{-3} M) were prepared by dissolving the lanthanide salt in water. An aqueous solution of 50×10^{-3} M $Eu(dpa)_3{}^{3-}$ was prepared following a standard procedure [15]. The sample of ca. 15×10^{-3} molal $Eu(dpa)_3{}^{3-}$ in BMIBr/water was prepared by mixing the appropriate volumes of aqueous $Eu(dpa)_3{}^{3-}$ with BMIBr/water. The final water content of this sample was not measured by Karl Fischer titration.

2.3. *Spectroscopic measurements*

The emission and excitation spectra were recorded using a LS-55 (PerkinElmer) luminescence spectrometer. In order to remove interference by the intrinsic ionic liquid fluorescence, emission and excitation spectra were recorded in phosphorescence mode with a 50 μs delay. Absorption measurements of BMIBr/water were recorded in a Cary 50 spectrophotometer. Luminescence decay measurements were recorded on custom-built instrumentation. The excitation source was a mercury arc lamp passed through a 0.1 M monochromator (Jobin-Yvon) to select the wavelength, and this excitation light was chopped by a variable-speed chopper (Stanford Research Systems, SR540) operating in the frequency range of 60–100 Hz. For excitation light at 580 nm, a N_2 pumped dye laser (Laser Photonics models LN1000/LN107) was used with laser dye, R590 (Exciton). The emission was collected at 90° to the excitation and focused on a 0.32 M monochromator (Jobin-Yvon, iHR320). The emission intensity was detected by a photomultiplier tube (Hammamatsu, R928) and recorded using a digitizing oscilloscope (Tektronix, TDS220) interfaced to a PC. For the emission spectra of Eu^{3+} samples, the asymmetry factor, *R*, has been determined. The asymmetry factor is the ratio of integrated intensities of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition. The uncertainty in the *R* value is ca. ± 10%.

3. Results and discussion

3.1. *Eu^{3+} in BMIBr/water*

Both $EuCl_3$ and $EuBr_3$ salts are soluble in the BMIBr/water. Both of the samples did seem to form solutions, because they are clear and show no evidence of a solid suspension or an emulsion. The typical strategy for lanthanide salt solubility in ionic liquids is to match the anions of the salt and IL ((e.g., $EuBr_3$ in BMIBr) [14]. Therefore, the solubility of $EuCl_3$ in BMIBr/water in this study is likely due to the presence of water as a co-solvent with the ionic liquid.

Fig. 1 shows a comparison of the emission spectra in the $^5D_0 \rightarrow {}^7F_{0-2}$ transition region of $EuBr_3$ salt in water, $EuBr_3$ in BMIBr/water, and $EuCl_3$ in BMIBr/water. The asymmetry factor for aqueous $EuBr_3$ is $R = 0.6$, which is not atypical for highly hydrated and highly symmetrical Eu^{3+} coordination environment. The asymmetry factors for each of the Eu^{3+} in the BMIBr/water show slightly larger values, $R = 1.6$ and 1.3, than the aqueous sample. Previous studies of $EuCl_3$ dissolved in BMICl/water [3] only show *R* values <2 for the octa- and nonahydrate europium species, which occur at water:BMICl mole to mole ratios above 2. The water:BMIBr ratio for the $EuBr_3$ and $EuCl_3$ samples in this study are closer to 1. Comparing the spectra of $EuBr_3$ and $EuCl_3$ in BMIBr/water in Fig. 1, there is an observable peak at 580 nm, $^5D_0 \rightarrow {}^7F_0$, in the $EuCl_3$ sample but not in the $EuBr_3$ sample. The observation of a $^5D_0 \rightarrow {}^7F_0$ transition may indicate a more complex coordination environment in the $EuCl_3$ sample ((e.g., Cl^- and Br^- exchange), but it is difficult to make that determination without detailed low-temperature spectroscopic data [3,16].

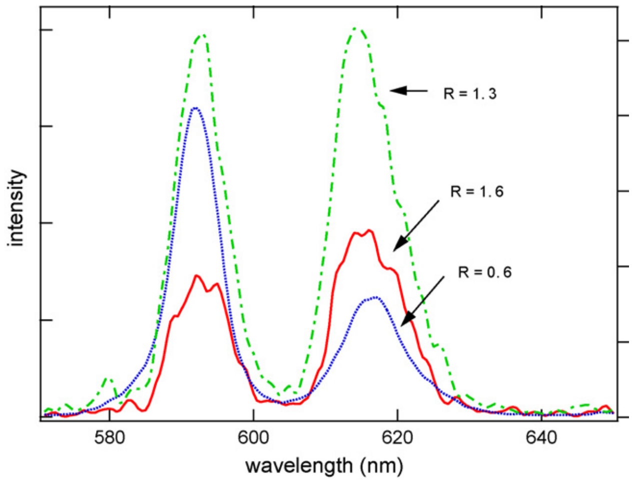

Fig. 1. Comparison of the emission spectra in the $^5D_0 \rightarrow {}^7F_{0-2}$ transition region of $EuBr_3$ in water (dotted line), $EuBr_3$ in BMIBr/water (solid line) and $EuCl_3$ in BMIBr/water (dashed-dotted line). The emission was recorded after a 50 μs delay to avoid interference from the intrinsic BMIBr fluorescence. The intensity scale is different for each spectrum to aid in comparison of the location and structures of the emission peaks. The asymmetry factors, *R*, are shown for each of the samples. The uncertainty in *R* is ca. 10%.

Due to the low luminescence signal and interference by luminescence from the ionic liquid, attempts to precisely determine the observed $^5D_0$ luminescence decay rate constant of $EuBr_3$ in BMIBr/water were unsuccessful. However, estimates based on luminescence decay measurements show that $k_{obs} > 10000\ s^{-1}$ for $EuBr_3$ in BMIBr/water, which is larger than the decay constant measured for aqueous $EuBr_3$ (presumably europium octa- or nonahydrate [17]), $k_{obs} = 6700\ s^{-1}$. Luminescence decay measurements exciting into this $^5D_0 \rightarrow {}^7F_0$ transition of $EuCl_3$ in BMIBr/water yield $k_{obs} = 10600\ s^{-1}$, which is consistent with the estimated decay constant for $EuBr_3$ in BMIBr/water. The highest k_{obs} shown in the study of $EuCl_3$ in BMICl/water is $<9000\ s^{-1}$ [3] for water:BMICl mole ratios > 4. Therefore, the R values and k_{obs} for Eu^{3+} seem to be more sensitive to water concentration in our BMIBr samples than in published BMICl samples [3].

Fig. 2 shows the excitation spectra for $EuBr_3$ and $EuCl_3$ in BMIBr/water. There is a surprising difference in the two spectra. Both spectra have broad excitation bands that seem to show sensitization of Eu^{3+} luminescence by the BMIBr. Previous studies on imidazolium ionic liquids have also shown sensitization

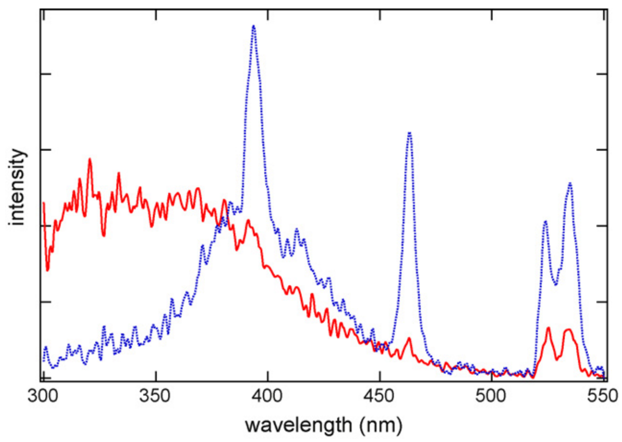

Fig. 2. Comparison of the excitation spectra of $EuBr_3$ (solid line) and $EuCl_3$ (dotted line) in BMIBr/water over the 300–550 nm wavelength range. The emission was monitored at 616 nm after a 50 μs delay to avoid interference from the intrinsic BMIBr fluorescence.

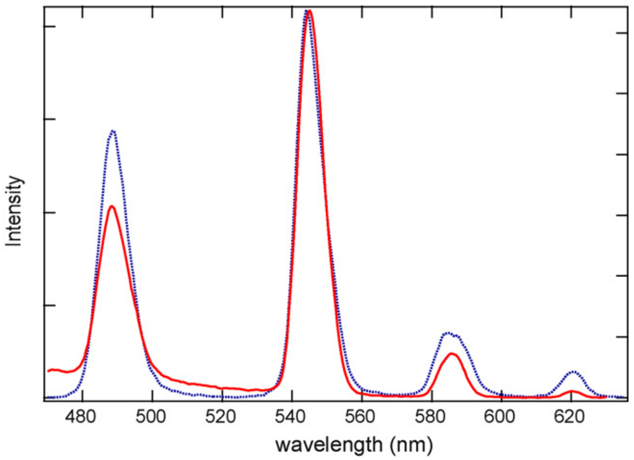

Fig. 3. Comparison of the emission spectra in the $^5D_4 \to {}^7F_{6-3}$ transition region of $TbCl_3$ in water (dotted line) and BMIBr/water (solid line). The emission was recorded after a 50 μs delay to avoid interference from the intrinsic BMIBr fluorescence. The intensity scale is different for each spectrum to aid in comparison of the location and structures of the emission peaks.

of Eu^{3+}luminescence [18]. However, the $EuBr_3$ sample shows a much broader excitation (300–450 nm) than the $EuCl_3$ sample (350–450 nm excitation). There is also a stark contrast in the observation of sharp 4f–4f Eu^{3+} transitions, where the excitation peaks at 396 and 465 nm are almost completely suppressed in the $EuBr_3$ sample. These differences could be due to a different solvent environment for $EuCl_3$ vs. $EuBr_3$ in BMIBr, or may just reflect different coordination environments.

3.2. *Tb^{3+} in BMIBr/water*

Similar to $EuCl_3$, $TbCl_3$ salts are soluble in the BMIBr/water mixture. The samples appeared (by visible inspection) to form a solution, and there was no evidence of a suspension or emulsion. Fig. 3 shows the emission spectra of $TbCl_3$ dissolved in water and in BMIBr/water over the $^5D_4 \to {}^7F_{6-3}$ transition region of Tb^{3+}. A comparison of the two spectra shows that the locations of all of the transitions are identical in aqueous vs. BMIBr/water, but the relative intensities show subtle differences. However, the density of Stark levels in the $^5D_4 \to {}^7F_{6-3}$ transitions make interpretation of the spectra with respect to Tb^{3+} coordination environment extremely difficult without low-temperature, high-resolution spectroscopy [16]. Fig. 4 shows the excitation spectrum of $TbCl_3$ in BMIBr/water.

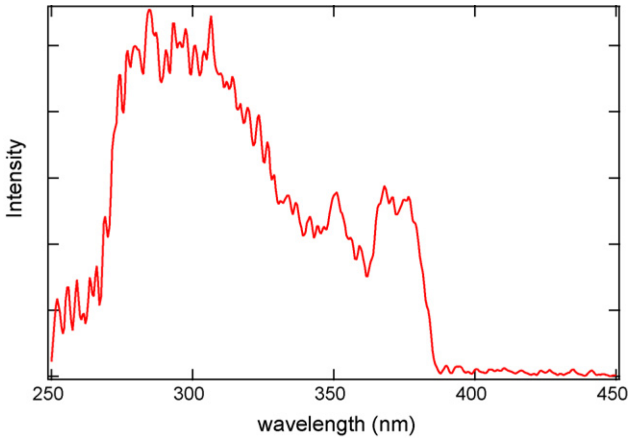

Fig. 4. The excitation spectrum of $TbCl_3$ in BMIBr/water over the 250–450 nm wavelength range. The emission was monitored at 545 nm after a 50 μs delay to avoid interference from the intrinsic BMIBr fluorescence.

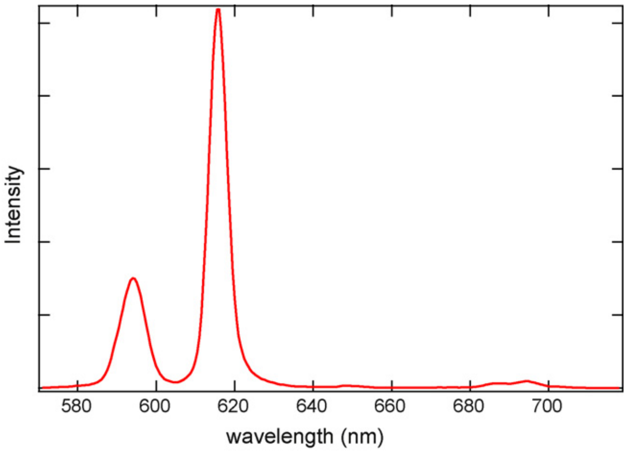

Fig. 5. The emission spectrum in the $^5D_0 \to {}^7F_{0-4}$ transition region of $Eu(dpa)_3{}^{3-}$ in BMIBr/water. The emission was recorded after a 50 μs delay to avoid interference from the intrinsic BMIBr fluorescence.

Similar to the excitation spectra of Eu^{3+} samples in BMIBr/water, the spectrum shows a broad excitation band indicating sensitization of Tb^{3+} emission by the BMIBr. This spectrum also shows Tb^{3+} 4f–4f excitation lines at ca. 350 ($^7F_6 \to {}^5D_2$, $^5G_5$,$^5L_9$) and 375 nm ($^7F_6 \to {}^5D_3$).

3.3. *$Eu(dpa)_3{}^{3-}$ in BMIBr/water*

Fig. 5 shows the emission spectrum of $Eu(dpa)_3{}^{3-}$ in BMIBr/$H_2$0 over the $^5D_0 \to {}^7F_{0-2}$ transition regions. The overall structure and relative intensities of the peaks are identical to the spectra of aqueous $Eu(dpa)_3{}^{3-}$ [15]. This indicates that the coordination environment of Eu^{3+} is unchanged in the ionic liquid mixture. Luminescence decay measurements give a $^5D_0$ decay rate constant for Eu^{3+}, $k_{obs} = 580 \pm 10\,s^{-1}$, which is also similar to that measured in aqueous solution. It appears that the presence of BMIBr shows no impact upon the spectroscopic properties of $Eu(dpa)_3{}^{3-}$. The sample through visible inspection appears to be a solution, and shows no evidence of an emulsion or suspension.

4. Conclusions

This study shows the results from excitation and emission spectra of a Tb^{3+}, and several Eu^{3+} compounds dissolved in BMIBr/water solutions. The excitation spectra show that the BMIBr ionic liquid does sensitize Eu^{3+} and Tb^{3+} luminescence. However, the Eu^{3+} and Tb^{3+}luminescence spectra are quenched by the ionic liquid, as evidenced by the large decay constants in Eu^{3+} (relative to aqueous and BMICl samples). It is also important to note that the emission spectra of the europium chloride and bromide salts dissolved in BMIBr/water were only observable after eliminating interference from ionic liquid fluorescence (time-delayed spectra). Additional studies ((e.g., EXAFS) are required to identify the exact Eu^{3+} and Tb^{3+} species present in the BMIBr/water. Many of the issues (i.e. large decay constants, small luminescence signals) could be due to the fact that the BMIBr ionic liquid used in this study is yellow, and clearly the spectroscopic properties of simple Eu^{3+} and Tb^{3+} salts are highly sensitive. In order to completely characterize the coordination and spectroscopic properties of lanthanide ions in BMIBr studies need to be conducted in colorless, anhydrous ionic liquids. However, the spectroscopic properties of $Eu(dpa)_3{}^{3-}$ complexes were insensitive to the presence of BMIBr, which indicates that they are plausible as intermolecular interaction probes even in binary solvent systems (BMIBr/water).

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