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Judd–Ofelt parameters of diglycolamide-functionalized calix[4]arene Eu^{3+} complexes in room temperature ionic liquid for structural analysis: Effects of solvents and ligand stereochemistry

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ABSTRACT

The complexation behavior of several diglycolamide (DGA)-functionalized calix [4]arene ligands (C4DGA) with Eu^{3+} in $C_8mimNTf_2$ (1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) was studied by time resolved laser fluorescence spectroscopy (TRLFS). The high intensity emission peaks of Eu^{3+} at 614 and 619 nm, which are due to the $^5D_0 \rightarrow {}^7F_2$ transition, sensitive to the local environment around Eu^{3+}, suggest that Eu^{3+} sits in a highly asymmetric environment. The metal-ligand stoichiometry of the complexes is 1:1, while there was no inner sphere water molecule around Eu^{3+}. The splitting pattern of the individual transitions of Eu^{3+} indicates that the local site symmetry around Eu^{3+} is C_{4V}. Though the emission characteristics of the complexes in $C_8mimNTf_2$ and a 1:5 acetonitrile-water mixture were similar, the smaller linewidth in $C_8mimNTf_2$ can be attributed to the restricted motion of the Eu^{3+} complex. Judd and Ofelt parameters (Ω_2, Ω_4) were calculated for all Eu^{3+}–C4DGA complexes. Steric crowding around the ligating sites decreases the proximity of Eu^{3+} with the carbonyl oxygens. This is evident from a decrease in the Ω_2 value, which is a signature of the increase in the bond length and concomitant decrease in the covalent interactions. Higher transition probabilities (A_{md}, A_{2ed}, A_{4ed}) of the Eu^{3+}–C4DGA complexes in $C_8mim \cdot NTf_2$ compared to a 1:5 acetonitrile-water mixture point to more mixing of the metal *f* orbitals with the ligand orbitals. The transition probability of the electric-dipole transition of $^5D_0 \rightarrow {}^7F_2$ is three times more than the magnetic-dipole transition probability and twice that of the electric-dipole transition of $^5D_0 \rightarrow {}^7F_4$. Alkyl substituents on the amidic nitrogen atoms increase the quantum efficiency as it decreases the additional non-radiative pathway.

1. Introduction

There is growing interest in room-temperature ionic liquids (RTILs) as "green" solvents for metal ion extraction including the actinides, which has great relevance in radioactive waste processing [1–5] Ionic liquids are composed of bulky, asymmetric organic cations (e.g., imidazolium, pyridinium, and ammonium derivatives) and anions, whose choice allows the physicochemical properties, such as the miscibility with water and viscosity, to be monitored and fine-tuned for effective applications. With hydrophobic anions such as PF_6^- or $(CF_3SO_2)_2N^-$, imidazolium-based ionic liquids form a separate phase with water and can thus be used for metal ion separations. Sr^{2+} extraction by solvents containing crown ethers in ionic liquids is one of the earlier works, which was promising for the possible application of ionic liquids in metal ion separations in the back end of the nuclear fuel cycle [6–9]. Literature shows exciting results on the extraction of actinides using ionic liquid-based solvent systems containing a variety of extractants such as diglycolamides (DGA) such as TODGA (*N,N,N′,N′*-tetraoctyldiglycolamide) [10–15], CMPO (carbamoylmethylphosphine oxide) [16–19], TBP (tri-*n*-butyl phosphate) [20], TTA (2-thenoyltrifluoro acetone) [21], etc. However, functionalized ionic liquids, termed as Task Specific Ionic Liquids (TSILs), even show extraordinary metal ion extraction properties [22–24]. The unusually high extraction of metal ions into an ionic liquid phase from a low acidity feed compared to that of molecular diluents is explained on the basis of a different extraction mechanism. In ionic liquid-based solvent systems, usually an ion-exchange mechanism predominates, while a solvation mechanism predominates in conventional molecular diluents [25]. Consequently, the nature of the extracted species, the kinetics and thermodynamics of the extraction, and the selectivity can differ significantly in ionic

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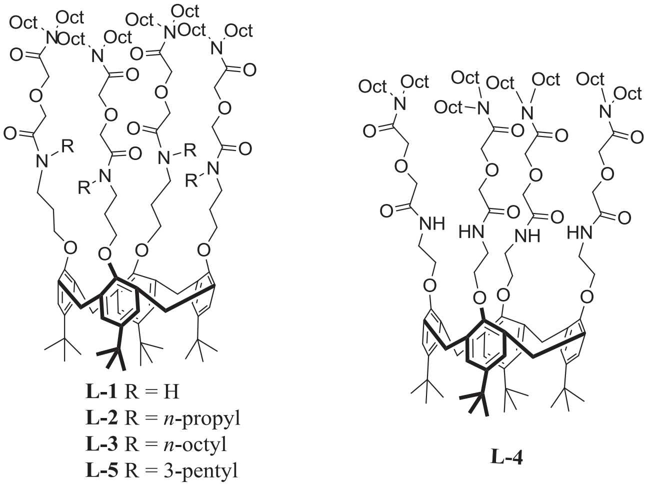

Fig. 1. Structures of diglycolamide-functionalized calix[4]arenes.

liquids vis-à-vis molecular diluents. Recently, we have reported several ionic liquid-based solvent systems containing calix[4] arene-based multiple DGA-functionalized ligands (C4DGA) or tripodal DGA (T-DGA) ligands for very efficient extraction of actinides with unusual selectivities [10–12]. The nature of the bonding in such bulky complexes is, however, not clearly understood.

The structure of the metal-ligand complexes needs to be analyzed to understand the nature of the bonding in the ionic liquid-based solvents. However, in view of the difficulty in obtaining single crystals, as an alternative, spectroscopic techniques are applied [26–31]. This study deals with the characterization of Eu^{3+}–C4DGA complexes in the ionic liquid $C_8mimNTf_2$ (1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) using time resolved laser fluorescence spectroscopy (TRLFS). Eu^{3+}, being a surrogate of Am^{3+} and a commonly studied metal ion with luminescence properties, is used to study the complexation with the different C4DGA ligands **L-1**–**L-5** (Fig. 1).

In addition to the effect of the medium, the role of structural modification of the C4DGA ligands, viz. alkyl substituents at the amidic nitrogen atom, spacer length (between the calix[4]arene platform and the ligating sites), on the luminescence properties of Eu^{3+} and the complexation nature were also investigated. Judd–Ofelt parameters, i.e. Ω_2, Ω_4, which indicate the measure of covalency of the bond between metal and ligating atom in a metal-ligand complex and the long range ordering effect, respectively [32–37], were calculated for all complexes and correlated with the steric hindrance around the ligating sites. The radiative and non-radiative lifetimes, branching ratios, the number of water molecules in the primary coordination sphere of the Eu^{3+} ion, and the probabilities of the observed transitions were also calculated.

2. Experimental

2.1. Eu(III)–C4DGA complexes

The C4DGA ligands **L-1**–**L-5** were synthesized as reported previously [38]. The ionic liquid, $C_8mimNTf_2$ (> 99% purity), was obtained from IoliTech, Germany, and was used as received. The complexes of Eu^{3+} in $C_8mimNTf_2$ were prepared by ensuring complete extraction. The extraction conditions were fixed as used in previous studies [10–12], i.e., the organic phase involved 5×10^{-4} M C4DGA **L-1**–**L-5** in $C_8mimNTf_2$, while the aqueous phase was 0.5 M HNO_3. For the Eu^{3+} luminescence studies in the aqueous phase, a 1:5 mixture of acetonitrile and water was used.

2.2. Instrumentation

Emission and excitation spectra were recorded on an Edinburgh F-900 Fluorescence Spectrometer in the 200–750 nm region with a Xe lamp as an excitation source, M-300 monochromators and a Peltier cooled photo multiplier tube as detector [17]. The acquisition and analysis of the data were carried out by F-900 software supplied by Edinburgh Analytical Instruments, UK.

3. Results and discussion

3.1. Local environment around Eu^{3+} ion

Emission spectroscopy is one of the important tools to probe the local environment around metal ions. The emission profiles of all the Eu^{3+}–C4DGA complexes in $C_8mimNTf_2$ appear to be similar with one peak at 593 nm (assigned to the $^5D_0 \rightarrow {}^7F_1$ transition), two peaks at 614 and 619 nm (due to the $^5D_0 \rightarrow {}^7F_2$ transitions), three peaks at 686, 698, and 701.5 nm (attributed to the $^5D_0 \rightarrow {}^7F_4$ transitions) (Fig. 2). The high intensity of the peaks due to the $^5D_0 \rightarrow {}^7F_2$ transition revealed that there is low symmetry around the Eu^{3+} ion. The assymetry factor, which is the signature of asymmetry around the Eu^{3+} ion with respect to inversion, was calculated using the following equation [39]:

$$A = I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1) \quad (1)$$

where, A is the asymmetry factor, $I(^5D_0 \rightarrow {}^7F_2)$ is the intensity of $^5D_0 \rightarrow {}^7F_2$, and $I(^5D_0 \rightarrow {}^7F_1)$ is the intensity corresponding to $^5D_0 \rightarrow {}^7F_1$ transitions. $^5D_0 \rightarrow {}^7F_1$ transition being magnetic-dipole transition, $I(^5D_0 \rightarrow {}^7F_1)$ is independent of the ligand field. The $^5D_0 \rightarrow {}^7F_2$ transition being a hypersensitive electric-dipole transition, $I(^5D_0 \rightarrow {}^7F_2)$ is hypersensitive to the ligand field. The assymetry factor values follow the trend Eu^{3+}–**L-1** > Eu^{3+}–**L-4** > Eu^{3+}–**L-3** > Eu^{3+}–**L-2** > Eu^{3+}–**L-5** for the complexes in $C_8mimNTf_2$ (Table 1), while the trend in the 1:5 acetonitrile-water mixture follows the order Eu^{3+}–**L-2** > Eu^{3+}–**L-1** > Eu^{3+}–**L-5** ~ Eu^{3+}–**L-3** (Table 2). In general, comparatively higher asymmetry factors were obtained for the metal-ligand complexes in the 1:5 acetonitrile-water mixture than in $C_8mimNTf_2$. A comparative study was carried out to understand the effect of medium on the

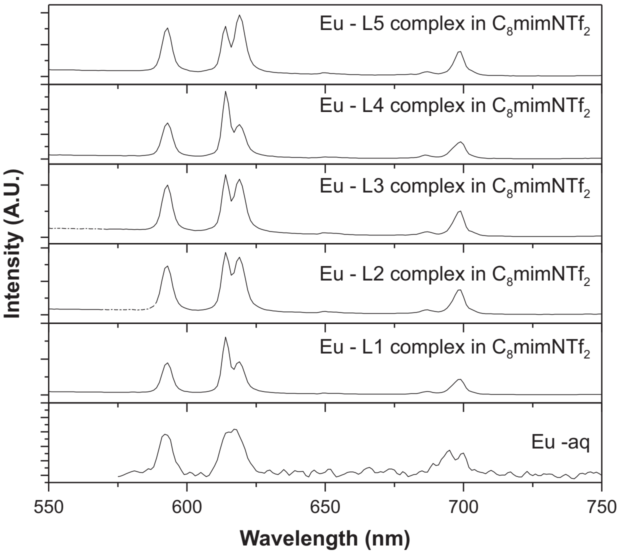

Fig. 2. Emission spectra of Eu-C4DGA complexes in $C_8mimNTf_2$.