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High-resolution steady-state and time-resolved luminescence studies on the complexes of Eu(III) with aromatic or aliphatic carboxylic acids

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ABSTRACT

Eu(III) luminescence spectroscopy, both in the steady-state and the time-resolved mode, is an appropriate technique to study the properties of complexes between heavy metal ions and humic substances (HS), which play a key role in the distribution of metal species in the environment. Unfortunately, room temperature luminescence spectra of Eu(III) complexes with aromatic and aliphatic carboxylic acids – model compounds of HS binding sites – are too broad to fully exploit their potential analytical information content.

It is shown that under cryogenic conditions fluorescence-line-narrowing (FLN) is achieved, and the highly resolved spectra provide detailed information on the complexes. Ten model ligands were investigated. Total luminescence spectra (TLS) were recorded, using the $^5D_0 \leftarrow {}^7F_0$ transition for excitation and the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions for emission. The energy of the excitation transition depends on the ligand involved and the structure and composition of the complex. For most ligands, discontinuities in the high-resolution TLS indicated that more species, i.e. distinct complex structures, coexisted in the sample. Selective excitation was performed to measure the species-associated luminescence decay times τ. The latter strongly depend on nearby OH oscillators from coordinating water molecules or ligand hydroxyl groups. Furthermore, the asymmetry ratios r, defined as the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, were calculated and the variation of the excitation energy E_{exc} with the splitting of the $^7F_1$ triplet (ΔE) was determined, which yielded the crystal field strength parameter $N_v(B_{2q})$, as well as the crystal field parameters B_{20} and B_{22}.

An in-depth analysis of the results is presented, providing detailed information on the number of coexisting complexes, their stoichiometry, the number of water molecules in the first coordination sphere and their geometry (symmetry point group).

1. Introduction

The fate, bioavailability and subsequently the toxicity of heavy metal ions are determined by their species distribution [1–5]. For example, knowledge regarding the transport and immobilization processes of radio nuclides in the vicinity of nuclear waste repository sites is a central issue in long-term safety assessments [6]. In soil and water compartments, humic substances (HS) represent a large part of the organic matter inventory; they play a key role in the species distribution of metal ions in the environment because they can form strong complexes [7–11]. Therefore, the analytical characterization of HS–metal complexes and understanding the processes involved in complexation are of utmost importance for the modelling of the ecological risks of heavy metals. Selective and sensitive analytical methods are indispensable to tackle this highly complex task.

The complexation of metal ions by HS can be monitored using spectroscopic methods such as fluorescence-based techniques. Measuring the degree of quenching of the intrinsic HS fluorescence was used to qualitatively and quantitatively describe the metal binding process [12]. However, the fluorescence properties of HS are very complex and data interpretation is hampered by the heterogeneous nature of HS. In addition, the possibility of intra- and inter-molecular energy and electron transfer processes inside the HS matrix has been discussed [13,14]. Even under ultra-low temperature conditions (at $T = 10$ K) only broadbanded spectra were found [15].

As an alternative to intrinsic HS fluorescence, the use of external luminescence probes such as europium (Eu(III)) or terbium (Tb(III)) ions is very promising for the investigation of metal complexation by HS. Moreover, Eu(III) is considered a natural analogue for actinides (An(III)), and is therefore an attractive surrogate when

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investigating actinide migration in the environment (e.g., in geological barriers of nuclear waste repository sites) [16]. Because of its outstanding luminescence properties, Eu(III) has been applied to probe the molecular environment in metal–HS complexes [17,18]. The Eu(III) luminescence spectra as well as the corresponding luminescence decay times are directly related to the properties of the metal complex formed. Unlike other experimental techniques that only provide information on an "average" complex, luminescence spectroscopy can provide specific information on the stoichiometry and geometry of the various complexes, depending on the experimental set up (vide infra) [17]. Complexation constants have been derived from sensitized Eu(III) emission and from changes in the asymmetry ratio r of the Eu(III) luminescence bands (relative intensity of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions) [19–21].

An inherent disadvantage of Eu(III) luminescence is that the extinction coefficients are extremely low due to a strong parity forbiddance for f–f transitions. The strongest transition in the UV/vis spectral range is found at $\lambda = 395$ nm with an extinction coefficient ε_{395} of about 3 M^{-1} cm^{-1} [22]. Nevertheless, Yoon et al. used the even weaker $^5D_0 \leftarrow {}^7F_0$ transition for excitation to gain information on the number of different Eu(III) complexes formed with HS [23]. Since this transition is non-degenerate, and therefore unlike other transitions involving the ^7F_x states not split by the crystal field of the ligands (STARK splitting), its energy $\Delta E(^5D_0 \leftarrow {}^7F_0)$ is characteristic for a specific complex [18,24].

However, in room temperature speciation experiments the usefulness of measuring this transition is limited due to spectral band broadening. In the present study, europium luminescence is probed using a more sophisticated approach: fluorescence line-narrowing (FLN) spectroscopy [25,26]. High-resolution luminescence spectra and decay curves are recorded at ultra-low temperatures (4.7 K), making use of energy-selective excitation by a narrow-banded, tuneable dye laser. A major difference with FLN studies of organic molecules is that, instead of vibronic bands of the same S_0–S_1 electronic transition, in the case of Eu(III) complexes different electronic transitions are probed: the non-degenerate $^5D_0 \leftarrow {}^7F_0$ transition is used for excitation while emission of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions is monitored. Nevertheless, the energies of these inhomogeneously broadened bands were found to be correlated, and line-narrowing was observed. The usefulness of this approach was demonstrated in recent papers [27–29].

The total luminescence spectrum (TLS) measured at 4.7 K contains a wealth of information, which is especially valuable for the investigation of samples containing mixtures of Eu(III) complexes. From the width of the $^5D_0 \leftarrow {}^7F_0$ transition (excitation spectrum) the degree of inhomogeneity (e.g., small variations in bond lengths, bond angles or water molecules in the second coordination sphere) can be assessed, whereas non-Gaussian shaped excitation spectra point at the occurrence of several distinct "species". As a first step towards FLN analysis of Eu(III) complexes with natural ligands such as humic acids, various hydroxybenzoic acids were investigated as model compounds, mimicking possible binding sites in HS [28,29]. Aliphatic acids and dicarboxylic acids were included to broaden the set of model ligands.

In the present paper an in-depth analysis of these systems is carried out with respect to: (i) the number of $^5D_0 \leftarrow {}^7F_0$ transitions observable in the excitation spectra, (ii) the asymmetry ratio r of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, and (iii) the variation of the excitation energy with the crystal field strength parameter $N_\nu(B_{2q})$ (referred to as jackstraws plots). Making use of the specific excitation wavelengths corresponding to the observed $^5D_0 \leftarrow {}^7F_0$ transitions in the TLS, species-selective luminescence decays were recorded in order to determine the number of water molecules and/or hydroxyl groups in the first coordination sphere for a particular complex.

On the basis of an integrated analysis of the excitation spectra, the emission spectra and the luminescence decay times, the number of different complexes coexisting in the sample, their stoichiometry and geometry (e.g., symmetry point group) were deduced.

2. Experimental

2.1. Chemicals

As model compounds for binding sites in HS, 10 different (hydroxy)benzoic acids and aliphatic acids were investigated. The relative positions of the hydroxyl- and/or carboxyl-group were systematically varied, in order to study the effect of complex formation and of the ligand structure on the ultra-low temperature luminescence spectra of Eu(III). Ligands used were *aromatic compounds:* 2-hydroxybenzoic acid (salicylic acid, 2HB), 3-hydroxybenzoic acid (3HB), 4-hydroxybenzoic acid (4HB), 3-methoxybenzoic acid (3MB), 4-methoxybenzoic acid (4MB), benzoic acid (BA), phthalic acid (benzene-1,2-dicarboxylic acid, PHA) and *aliphatic compounds:* glycolic acid (hydroxyacetic acid, GL), 3-hydroxy propionic acid (3HP), glutaric acid (*n*-pentanedioic acid, GA). As reference systems we used $EuCl_3 \cdot 6H_2O$ crystals and a 0.2 M aqueous $EuCl_3$ solution containing 0.1 M of $NaClO_4$. The chemicals were purchased from Aldrich with the highest purity available and used as received.

Stock solutions of Eu(III) ($EuCl_3 \cdot 6H_2O$) and model compounds (ligands) were prepared in deionized water and the pH was adjusted to (5 ± 0.1) using HCl or NaOH, as required [30]. The concentration of the stock solutions was 2×10^{-1} M; these were then mixed to yield a molar ratio of Eu(III):ligand = 1:9 ($C_{Eu(III)} = 0.02$ M, $C_{ligand} = 0.18$ M). The nine-fold excess in ligand concentration was chosen in order to minimize the concentration of free Eu(III) ions. Under those conditions the fraction of complexed Eu(III) is >97%, even for very low $\log \beta$ values of 2–3 [31–33]. After mixing, the samples were allowed to equilibrate for at least five days at 20 °C [29]. In-between measurements, the samples were stored in the dark at room temperature.

2.2. Instrumentation

For FLN spectroscopy, sample solutions were transferred to quartz tubes (40 mm length × 4 mm o.d. × 2 mm i.d.; volume ca. 100 μL), and sealed with rubber septums. Up to four samples could be cooled simultaneously to 4.7 K in a lab-built sample holder, mounted on a closed-cycle helium refrigerator (SRDK-205 cryostat; Janis Research Company, Wilmington, MA, USA). The samples were excited using a dye laser (LPD 3002; Lambda Physics, Göttingen, Germany) pumped by a XeCl excimer laser (LPX 110i; Lambda Physics, Göttingen, Germany). Coumarin 153 (Radiant Laser Dyes & Accessories GmbH, Wermelskirchen, Germany) was used as laser dye. The laser was operated at 20 Hz with a pulse width of 3 ns. The Eu(III) emission was collected at a 90° angle relative to the excitation light by two 10 cm F/4 quartz lenses and focused on the entrance slit of a triple monochromator (Spex 1877; Edison, NJ, USA). For detection an intensified charged-coupled device (iCCD) camera (iStar DH720-25U-03; Andor Technologies, Belfast; Northern Ireland) was used in the gated mode. In order to obtain adequate stray light suppression, delay and gate width of the iCCD were set to 1 μs and 10 ms, respectively. The achieved spectral resolution in the emission dimension was 0.1 nm (3 cm^{-1}) in a total spectral detection window of 37 nm. For wavelength calibration a neon arc lamp was used. Typically, the excitation wavelength was scanned over the spectral range 577 nm < λ_{exc} < 581 nm (17,331 cm^{-1} > E_{exc} > 17,212 cm^{-1}) and the luminescence was observed in the spectral range between 585 nm < λ_{em} < 622 nm (17,094 cm^{-1} > E_{em} > 16,077 cm^{-1}), covering