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Photochemical characterization of uranyl interaction with acetic acid

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ABSTRACT

Aqueous perchloric acid solutions containing 1×10^{-4} M of U(VI) and acetic acid at different concentrations (from 0 up to 0.6 M) are studied by time-resolved laser-induced luminescence spectroscopy (TRLLS) at pH 1.5, 2.0 and 2.5. The quenching of uranyl luminescence is observed. The graphs giving U(VI) luminescence intensity, as a function of dissociated and non-dissociated acetic acid form concentrations are constructed at the different pH values to point out the interacting ligand species. Acetate ions are demonstrated to be responsible for the luminescence quenching. Stern–Volmer analysis gives the dynamic quenching rate constant value (k_q) $(1.0 \pm 0.2) \times 10^9$ L M^{-1} s^{-1} at ionic strength (μ) 0.05 M (pH 2.0). The bimolecular excited-state process is shown to be diffusion-controlled as k_q is practically identical to the diffusion rate constant as calculated for uranyl and acetate species. With an increase of acetate concentration (from 1×10^{-4} M), static quenching occurs in addition to the dynamic quenching. The formation of a non-luminescent complex between uranyl and acetate is supported (with 1:1 stochiometry). The stability constant values for the first complex species ($UO_2CH_3COO^+$) are obtained at different ionic strengths. Extrapolation to $\mu = 0$ by the specific ion interaction theory (SIT) gives log $\beta_1{}^\circ = 2.95 \pm 0.08$ at 293 K. From 1.5×10^{-3} M of acetate concentration, the decay curves became biexponential and shorter lifetime appears. The U(VI) luminescence intensity is not decreased anymore and the bathochromic shift of peak maxima is observed. Most probably, this indicates the formation of the second complex species of U(VI) with two acetate ligands. These species give luminescence emission.

1. Introduction

Uranyl ions exhibit a highly structured luminescence spectrum in aqueous solutions [1–6]. The luminescence spectrum of uranyl have the six bands at 585, 558, 533, 509, 488 and 470 nm in noncomplexing media (an acidic perchlorate medium) [2]. They reflect the symmetrical vibration of U–O bond in the ground electronic state. The luminescence of uranyl is mainly due to the photon emission from lowest electronically excited state of the uranium nonbonding 5f orbitals ($5\sigma_u$ and $5\phi_u$) [4]. The luminescence properties of uranyl allow us to obtain the rich information about the uranyl speciation in solutions. Time-resolved laser-induced luminescence (fluorescence) spectroscopy becomes an advantageous experimental method for study of actinide chemistry [7–9]. In the literature, the term "fluorescence" is often used to describe the luminescence of uranyl in aqueous solutions. The lifetime of excited state of uranyl is at minimum in the level of 10^{-6} s in aqueous solutions and the luminescence is generally assigned to the lowest excited triplet state of uranyl. Thus, the luminescence of uranyl is phosphorescence [6,10].

It is interesting to use the luminescence properties of uranyl ions to study the interaction of natural organic matter with uranyl [11,12]. The complexation of radionuclide with natural organic matter can significantly affect their migration in the natural aqueous media [13–16]. To understand the regularity of change of luminescence properties of uranyl in the presence of complicated organic matter, it is entertaining to study the interaction of uranyl with simple organic acid.

Acetic acid is the smallest organic acid with a carbon chain. It can represent the most simple model substances for humic acids which can occur as humic acid building blocks and simulate their structure and functionality [13,17,18]. Humic acids are the principal components of humic substances, which are the major constituents of

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organic matter. Acetic acid can be also the product of chemical industry [19,20] and may be issued from some technological processes [21].

Uranyl forms the complex species with acetate. Complex equilibriums between uranyl and acetate are studied in the number of papers [22–38]. The spectrophotometry [22–24], potentiometry [22,25–30], ion exchange [24,31,32], solvent extraction [33–35], polarography [36] and affinity capillary electrophoresis [37,38] have been employed. The data obtained are reviewed in [37,38]. Although the luminescent properties of uranyl are often used to study its complexation with different types of organic ligands (for example, malonate [39], hydroxamic and benzoic acids [40], oxalate, citrate [41], glucose [42] and glycine [43]), to the best of our knowledge, the complexation of uranyl with acetate has never been studied by luminescent methods.

The aim of the present work is to study the luminescence properties of uranyl in the presence of acetic acid, to identify the complex formation, calculate the stability constant of complex species formed and to extrapolate the stability constant values obtained to zero ionic strength (μ). The obtained values are compared with known literature data.

2. Experimental

2.1. Chemicals and solutions

All chemicals used are of analytical reagent grade. The stock $UO_2(ClO_4)_2$ solution (0.1 M in 0.63 M $HClO_4$) is obtained by dissolving $UO_2(NO_3)_2{\cdot}6H_2O$ (>99% FLUKA puriss) in 12 M $HClO_4$ (MERCK Suprapur) and evaporating the resulting solution to almost dryness on a sand bath. The residue is dissolved in concentrated $HClO_4$ and evaporated again. This last operation is repeated 3 times. Glacial acetic acid ($\geq$99.99%) is supplied by Sygma–Aldrich. Concentrated perchloric acid (60% solution from Sigma–Aldrich) is diluted in water to the requested concentration. The exact concentration is determined by acid–base titration with certified NaOH solution. Sodium perchlorate (99%) is provided by Merck. All solutions are prepared with deionised water (Millipore direct Q, $R = 18\,M\Omega$).

In order to avoid hydrolysis and/or polymerization of the uranyl ion, that could potentially lead to the formation of additional excited species and/or to the modification of uranyl intensity spectra, we work with perchloric media in the range of pH from 1.5 to 2.5. At such pH values and uranyl concentration of 1×10^{-4} M, the contribution of hydrolysed and polymeric species to U(VI) luminescence spectra is insignificant [44,45].

2.2. Apparatus

2.2.1. Time-resolved laser-induced luminescence spectroscopy

TRLLS experiments are carried out using a Continuum® Nd:YAG laser (frequency 10 Hz, pulse duration of about 7 ns) as the excitation source coupled with a Panther® OPO. The detection is made by a Spectra-Pro-300 monochromator (Acton Research corporation®) coupled with a CCD camera (Princeton Instruments®). The excitation wavelength is chosen at 430 nm (at maximum of U(VI) luminescence intensity) and the laser power is about 1.5 mJ. Emission spectra are recorded using the software WINSPEC (Princeton Instruments®). The luminescence spectra have a resolution better than 0.5 nm. The error on the measured luminescence intensity is less than 5%.

All of the luminescence intensity measurements are carried out on non aerated solutions in a quartz cuvette at temperature 20 ± 1 °C. Every measurement is repeated at least 3 times.

The luminescence spectrum integration (from 450 to 600 nm) and luminescence decay curves are calculated with the Origin Pro® 7.5 software program.

All concentration and constant calculations are done with the EXCEL® software program. The solver module is used for fitting experimental points by least squares curve method.

For the speciation diagram construction, the MEDUSA software (KTH Royal Institute of Technology, Chemistry Department) is used.

2.2.2. pH measurements

A pH-meter GLP-21 (Crison, France) and a combination electrode are used for pH measurements after calibration against NIST standards (4.01 and 7.00). An aliquot of solution is used for each measurement. The errors of pH values of measured solutions are ±0.05.

3. Results

3.1. Emission spectra of U(VI) in the presence of acetic acid

Luminescence spectra of 1×10^{-4} M U(VI) in the presence of different concentrations of acetic acid (from 0 to 0.5 M) at pH 1.5 ($HClO_4$) and at an ionic strength 0.05 M ($NaClO_4$) are presented in Fig. 1. One can distinguish the six emission bands at 470, 488, 509, 533, 558 and 585 nm in the absence of acetic acid. This spectrum corresponds to non complexed uranyl ions $UO_2(H_2O)_5^{2+}$ [2]. The intensity of the spectra emission is found to decrease with the increase of acetic acid concentration from 5×10^{-4} M to 0.5 M. The positions of the main emission bands of the luminescence spectra of uranyl do not change with the increase of the acetic acid concentration. The similar situation is observed at pH 2.0 and pH 2.5. The intensities of the spectra emission are found to decrease with the increase of acetic acid concentration up to about 0.3 M at pH 2.0 and up to about 0.1 M at pH 2.5. The positions of the main emission bands of the luminescence spectra of uranyl do not change.

With the increase of acetic acid concentration from 0.3 M (pH 2.0) and from 0.1 M (pH 2.5), we do not observe a quenching of U (VI) intensity. Moreover, the U(VI) intensity is slightly increased and we observe bathochromic shift of peaks (Fig. 2).

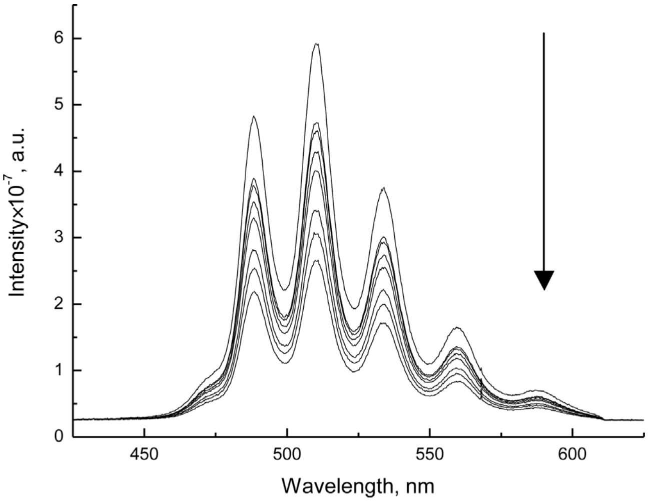

Fig. 1. Luminescence spectra of 1×10^{-4} M of U(VI) in the presence of different acetic acid concentrations from 0 to 0.05 M (from top to bottom); pH 1.5; $\mu = 0.05$ M ($NaClO_4$); 2000 accumulations; initial delay: 0.15 µs; width: 20 µs.