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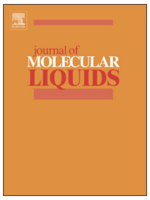

Investigation of the speciation of uranium(VI) in concentrated phosphoric acid and in synergistic extraction systems by time-resolved laser-induced fluorescence spectroscopy (TRLFS)

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ABSTRACT

The speciation of uranium(VI) present in aqueous solutions of 0.73–7.08 mol.L^{-1} phosphoric acid or extracted from these solutions in various organic phases was investigated by time-resolved laser-induced fluorescence spectroscopy (TRLFS). The organic phases consisted of bis-(2-ethyl-hexyl) phosphoric acid (D2EHPA), bis(1,3-dibutyloxypropan-2-yl) phosphoric acid (BiDiBOPP) and synergistic mixtures of tri-*n*-octylphosphine oxide (TOPO) or di-*n*-hexyl octyl methoxy phosphine oxide (di-*n*-HMOPO) with D2EHPA or BiDiBOPP in Isane IP 185 (an aliphatic diluent). The present paper indicates that uranium(VI) exists as a unique species in aqueous solutions of 0.78–7.08 mol.L^{-1} H_3PO_4 likely as $UO_2(H_3PO_4)_n(H_2PO_4)_m^{2-m}$ where n + m = 3, and that a predominant uranium(VI) species (more than 90%) is extracted by the D2EHPA/TOPO synergistic mixture. This species, whose formula is likely $UO_2(HL)_2L_2$TOPO with HL = monomeric D2EHPA and L = deprotonated form of D2EHPA, is characterized by the fact that the TOPO molecule is located in the first solvation shell of uranium(VI) as also confirmed by DFT calculations. Furthermore, TRLF spectra of uranium(VI) in D2EHPA/di-*n*-HMOPO and BiDiBOPP/di-*n*-HMOPO are quite different from those obtained with the D2EHPA/TOPO mixture. Indeed, the vibronic peaks of uranium(VI) TRLF spectra have partially (D2EHPA/di-*n*-HMOPO) or completely (BiDiBOPP/di-*n*-HMOPO) disappeared, which could be due to the presence of oxygen atoms in the hydrophobic chains of BiDiBOPP and di-*n*-HMOPO. As in the case of the D2EHPA/TOPO mixture, the fluorescence lifetime of uranium(VI) in the BiDiBOPP/di-*n*-HMOPO mixture indicates that uranium(VI) is extracted by this mixture from 5.3 mol.L^{-1} H_3PO_4 as a unique or at least a predominant species.

1. Introduction

A revival interest concerns the extraction of uranium from wet phosphoric acid (WPA) as phosphate rocks are considered to be an important source of uranium [1] and because environmental regulations will likely evolve so that fertilizers do not contain uranium. Solvent extraction is the technology of choice for extracting uranium from WPA. The Oak Ridge National Laboratory developed the first process for the recovery of uranium(VI) from WPA at the end of 1960's. This process used a mixture of 0.5 mol.L^{-1} bis(2-ethylhexyl)phosphoric acid (D2EHPA) and 0.125 mol.L^{-1} tri-*n*-octylphosphine oxide (TOPO) diluted in kerosene [2,3]. Several synergistic extraction systems were developed to replace the reference system, i.e. bis(2-ethylhexyl) phosphoric acid (D2EHPA) and tri-*n*-octylphosphine oxide (TOPO) diluted in kerosene [2]. For instance, the extraction properties of uranium(VI) from concentrated phosphoric acid by mixtures of bis(1,3-dibutyloxypropan-2-yl) phosphoric acid (BiDiBOPP) and di-*n*-hexyl octyl methoxy phosphine oxide (di-*n*-HMOPO) [22] or dinonylphenyl phosphoric acid (DNPPA) and tri-*n*-octylphosphine oxide (TOPO) [4,5], as well as (2-ethylhexyl) phosphonic acid or mono (2-ethylhexyl) ester (PC88A) in mixture with di-butyl butyl phosphonate (DBBP) [6] were investigated.

More recently, Beltrami et al. [7–10] studied the influence of the structure of phosphoric and thiophosphoric acids, phosphinic and thiophosphinic acids as well as the influence of the structure of

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solvating agents in synergistic mixtures on the extraction properties of uranium(VI) from WPA [8,9]. The extraction equilibria and the speciation in organic phase are particularly important to understand the origin of the selectivity and the mass transfer of uranium(VI) from phosphoric acid into the extraction solvent. Slope analysis method [11–13], UV spectroscopy [14], infrared spectroscopy [15,16], small angle X-ray and neutron scattering as well as static and dynamical light scattering measurements [17] were mostly used to study the speciation of uranium(VI) in D2EHPA/TOPO. Conversely, no paper concerns the use of Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS) to investigate the speciation of uranium(VI) in extraction solvents contacted with concentrated phosphoric acid. Likewise, no paper deals with TRLFS studies of the speciation of uranium in aqueous concentrated phosphoric acid (0.73–7.08 mol.L^{-1}) whereas literature reports such studies in diluted phosphoric acid (10^{-4} to 10^{-1} mol.L^{-1}) [18–21].

In this paper, the speciation of uranium(VI) in aqueous solutions of 0.73–7.08 mol.L^{-1} phosphoric acid as well as in various organic phases equilibrated with these phosphoric acid solutions has been investigated by TRLFS. The organic phases consisted of 0.5 mol.L^{-1} D2EHPA or BiDiBOPP in mixture with 0.125 mol.L^{-1} TOPO or di-*n*-HMOPO in Isane IP 185 (Scheme 1), i.e. D2EHPA/TOPO, D2EHPA/di-*n*-HMOPO, BiDiBOPP, BiDiBOPP/TOPO and BiDiBOPP/di-*n*-HMOPO mixtures.

2. Experiments

2.1. Reagents

Bis-(2-ethylhexyl)-phosphoric acid (Aldrich, purity > 97%), tri-*n*-octylphosphine oxide (Fluka, purity > 90%) and Isane IP 185 (Total Fluides, a 100% C_{11}–C_{14} isoparaffinic diluent with flash point and boiling range equal to 66 °C and 187–206 °C, respectively) were used as received. Bis(1,3-dibutoxyprop-2-yl) phosphoric acid (BiDiBOPP) and di-*n*-hexyl octyl methoxy phosphine oxide (di-*n*-HMOPO) were synthesized as reported elsewhere [8,22].

Aqueous phosphoric acid solutions ranging between 0.73 and 7.08 mol.L^{-1} and containing 0.34 g.L^{-1} uranium(VI) [$1.43\cdot10^{-3}$ mol.L^{-1}] were prepared by diluting concentrated phosphoric acid (VWR, AnalanR Normapur, purity > 85%) and 0.1 mol.L^{-1} uranyl nitrate (Fluka) with water (resistivity > 18 MΩ.cm) purified with a milli-Q Gradient system from Millipore Corporation.

The influence of the nitrates on the uranium(VI) extraction equilibria was considered as negligible as the nitrate concentration in the feed solution was very low compared to that of phosphoric acid and the complexing power of nitrates towards uranium(VI) is weak [23].

2.2. Preparation of the organic phases for TRLFS analyses

Liquid–liquid extraction of uranium(VI) (initially 0.34 g.L^{-1}) from phosphoric acid solutions by 0.5 mol.L^{-1} phosphoric acid diesters (D2EHPA or BiDiBOPP) alone or in mixture with 0.125 mol.L^{-1} phosphine oxide (TOPO or di-*n*-HMOPO) in Isane IP 185 was carried out by mixing the two phases during 1 h with a phase volume ratio O/A = 1, at (25.0 ± 0.2) °C. Preliminary experiments showed that 1 h was sufficient to reach the extraction equilibria.

The aqueous and organic phases were then separated in a separating funnel after centrifuging for 10 min at 3000 rpm with a Universal 16 centrifuge. The organic phase was then filtered with Whatman 1PS phase separators.

Water content was measured by the Karl Fischer titration method with a Mettler-Toledo coulometric Titrator (V20).

Uranium concentrations in aqueous solutions were determined by ICP-AES using a Varian Vista Pro spectrometer with a precision of ±5%. Before analyses, the aqueous solutions were filtered with a hydrophilic filter (Minisart NML 16555K, cellulose acetate, 0.45 µm, d = 28 mm). The concentrations of uranium(VI) in organic phases were deduced from mass-balance calculations, i.e. from the difference between the uranium concentration in aqueous phase before and after extraction. The distribution coefficients of uranium(VI) [$D_{U(IV)}$] were calculated from the ratio of the concentration of uranium in the organic phase to that in the aqueous phase and the uncertainties on the uranium(VI) distribution coefficients are estimated as 10%.

2.3. Time-resolved laser-induced fluorescence spectroscopy (TRLFS)

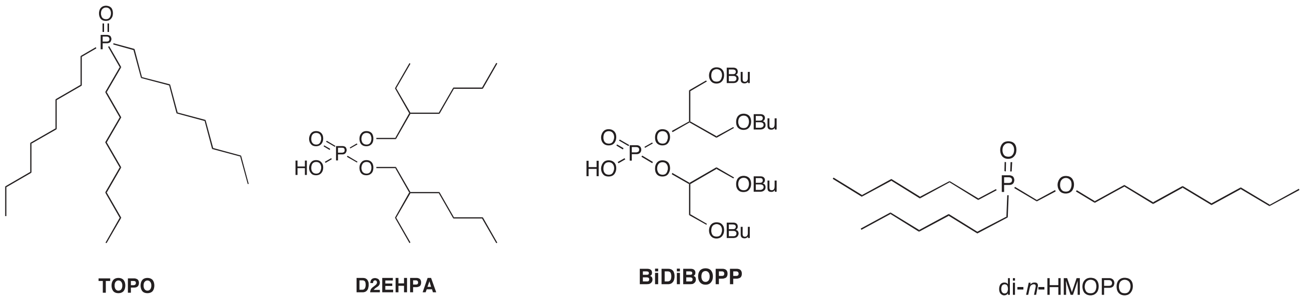
Uranium(VI) fluorescence spectra and decay curves in aqueous and organic solutions were studied by Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) at room temperature, using a tunable OPO Panther® Continuum pulsed laser at incident wavelength of 430 nm and 3 mJ energy. The detection was made by means of a Spectra-Pro®-300 monochromator (Acton Research Corporation® coupled with a Princeton Instruments® CCD Camera).

All of the TRLF spectra were recorded at the same temperature (22 °C) between 450 and 600 nm by using 2 mL quartz glass cuvettes. The fluorescence decay curves of uranium(VI) in organic phases were obtained with a gate width of 5 µs, a delay range between 0.2 and 5 µs whereas the gate width was 1 µs and the delay ranges between 0.2 and 1000 µs for the aqueous phases. For each delay time, each luminescence spectrum was recorded three times, and for each spectrum 100 accumulations were averaged. Fluorescence lifetimes were calculated by fitting the fluorescence decay curves with the following exponential function using the IGOR Pro® software:

$$I(t) = A_o + \sum_i A_i e^{-t/\tau_i} \qquad (1)$$

where t, A_o, A_i and τ_i represent the time with respect to the beginning of the laser pulse, the background signal level (the fluorescence intensity for an infinite delay), the pre-exponential signal factors and the lifetime of uranium(VI) species i, respectively. The uncertainties on the calculated lifetimes were estimated to be around 10%.

The TRLFS spectrum of 0.02 M uranium(VI) in perchlorate acidic solution was recorded and used as standard spectrum. Uranyl solution



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Scheme 1.

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