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A screening method of uranyl extractants in H_2SO_4 solutions

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ABSTRACT

A UV–Vis spectrophotometric and colorimetric screening method was developed for the selection of powerful and selective ligands for the uranyl ion in sulfuric acid media. The coordinating properties of a series of molecules (mono and bisphosphonate) toward UO_2^{2+} were examined through ligand displacement reactions observed by UV–visible from the $\{\mathbf{ArzH_4}–UO_2\}^{2-}$ reference complex where $\mathbf{Na_2ArzH_6}$ is a chromogenic molecule displaying a strong affinity for uranium. Uranium/iron selectivity was evaluated by recovering the screening data from two independent sets of experiments using two different chromogenic chelates: arsenazo III for uranium(VI) and BrPADAP for iron(III). As a result, two bisphosphonate ligands among a set of more than 50 phosphonate molecules were found to display a good affinity for UO_2^{2+} and relevant U/Fe selectivity at pH = 2.1.

Industrial extraction of uranium is based on different processes derived from pyrometallurgy, precipitation or ion exchange.[1] Uranium mining is currently recovered by leaching ores with concentrated sulfuric acid aqueous solutions (pH < 2), and mostly extracted with mixtures of tertiary amines in kerosene.[2] However, concomitant extraction of elements (like Fe, Al, Si, Mo, V, and Zr) contained in the uranium acidic solutions[4] and degradation of the extractants limit the efficiency of the process.[3,4] Beside economical and environmental aspects of the processes, major improvement for liquid–liquid uranium extraction would be the finding of new chelating molecules, much more robust toward acidic and oxidizing conditions, and displaying both stronger affinity and selectivity for the uranyl ion (UO_2^{2+}).

At that time, the search of specific extractants for metal ions is rather empirical and requires laborious experimental works. The use of a single step method to detect rapidly, from a wide range of molecules, those displaying the strongest affinity and/or selectivity for a targeted metal ion would offer considerable interest with potential industrial applications as in the nuclear field.

A rapid detection, by screening methods, of uranium extractants in sulfuric acid media is highly desirable. In recent years, such a methodology was developed[5,6] for uranium decorporation in biological media[7–9] and several polydentate dipodal and tripodal bisphosphonate molecules have been successfully tested.[6,10] However, these methods were inappropriate for the evaluation of the uranyl-binding properties of ligands at pH < 4.

Here, we report a colorimetric method dedicated to the selection of ligands with strong affinity for U(VI) in sulfuric acid media and at low pH (pH = 2.1). The principle is based on a competition reaction between the initial blue complex $\{\mathbf{ArzH_4}–UO_2\}^{2-}$, obtained from arsenazo III ($\mathbf{Na_2ArzH_6}$, Fig. 1) and UO_2^{2+}, and an additional ligand. A stronger ligand than $\mathbf{ArzH_4}$ will cause partial or total displacement of this latter giving rise to a change of color from blue to pink (free $\mathbf{ArzH_6^{2-}}$) at the utmost. Quantification of the displacement rate of $\mathbf{ArzH_4}$, which would give an overview of the affinity of a ligand for U(VI), can be deduced from UV visible spectrophotometry studies, by monitoring the characteristic absorbance of $\{\mathbf{ArzH_4}–UO_2\}^{2-}$.

A similar strategy with the orange **BrPADAPH** chromophore (Fig. 1) and the corresponding violet complex $\{\mathbf{BrPADAP}–Fe^{III}\}^{2+}$

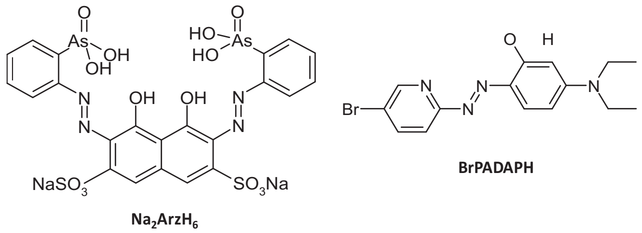

Figure 1. Arsenazo III ($\mathbf{Na_2ArzH_6}$, pink) and **BrPADAPH** (orange) molecules.

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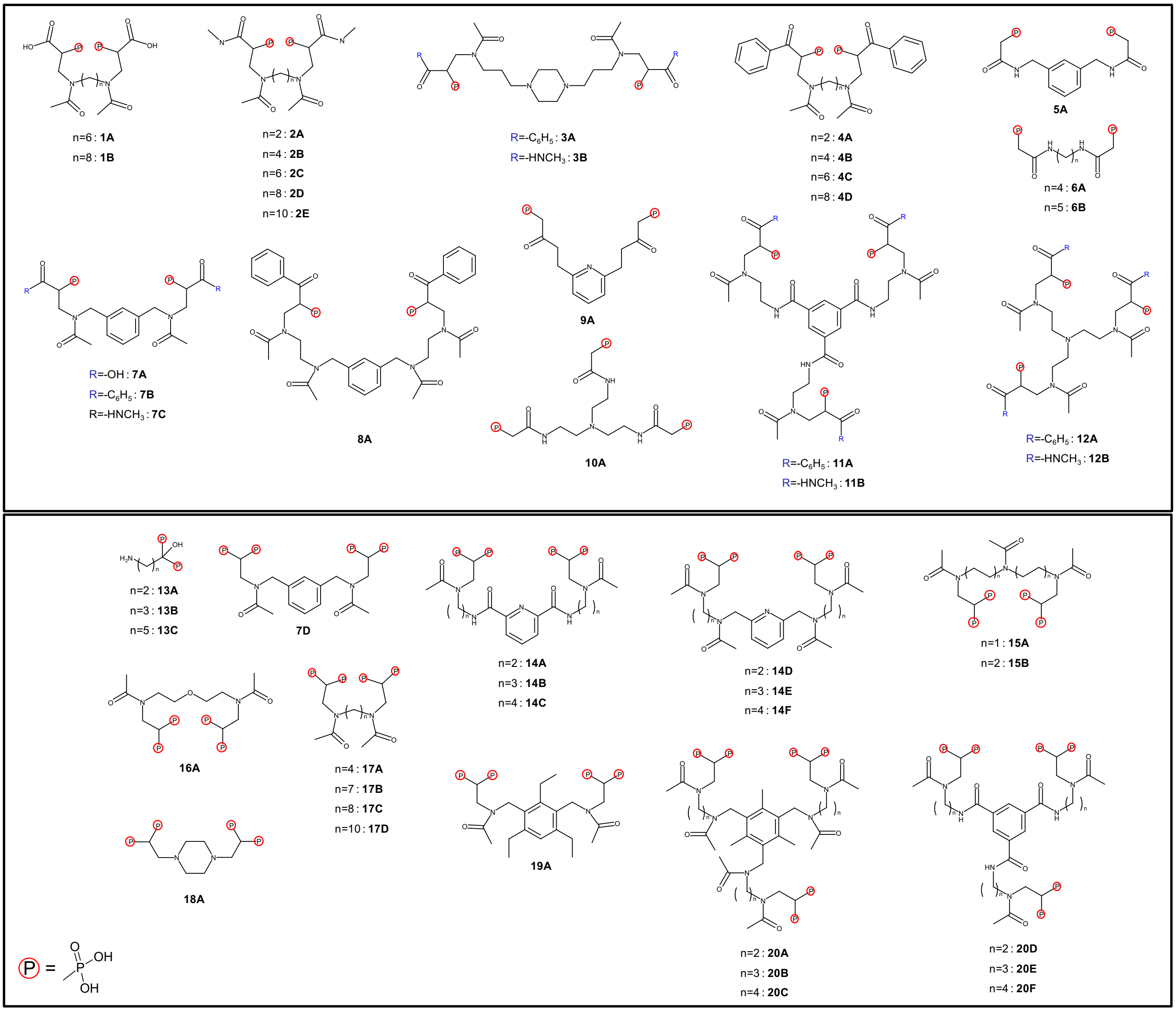
($\log \beta_{1,1} = 6.3 \pm 0.3$) of lesser stability than $\{\textbf{ArzH}_4\text{–UO}_2\}^{2-}$ ($\log \beta_{1,1} = 7.3 \pm 0.3$), was applied for the detection of ligands having poor affinity for Fe^{3+} ion. Thus, for a given ligand, these colorimetric methods coupled with UV–visible measurements permit to draw its respective affinity for each ion and to gauge the corresponding Fe^{3+}/UO_2^{2+} selectivity.

Mono and bisphosphonate molecules are known as strong uranophiles.[11] The bisphosphonate chelating function of those ligands is well adapted to chelation under acidic media since its first pK_a value is around 2.[12] The screening method has been further applied, in diluted sulfuric acid, to 51 of these molecules (Scheme 1) in order to determine and compare their affinity for uranium (% displacement of $\textbf{ArzH}_4$) and U(VI)/Fe(III) selectivity.

Choice of Na_2ArzH_6 as the chromophore for uranyl

The principle of our method is based on the dissociation of a preformed chromogenic uranyl complex after the addition of another coordinating agent. It requires a well-characterized reference chelate having a good affinity for uranium in order to form a very stable complex in acidic media and which displays strong UV–Vis absorption ($\lambda_{max} > 400$ nm to have a colorimetric test). Arsenazo III ($\textbf{Na}_2\textbf{ArzH}_6$) is a well known indicator for uranium(VI),[13,14] and seemed to us the most suited chromophore (Fig. 2). Indeed, the first crucial constraint is that the $\{\textbf{ArzH}_4\text{–UO}_2\}^{2-}$ complex must show a strong characteristic UV–vis frequency which decreasing could be monitored in the presence of a competitive ligand. In diluted H_2SO_4 solution (5 mM, pH = 2.1), formation of $\{\textbf{ArzH}_4\text{–UO}_2\}^{2-}$[14] is observed by an UV–vis broad band at 650 nm (Fig. 2a). This is the unique species as proved by a clear isobestic point at 580 nm during addition of up to 1 equiv UO_2^{2+} into a solution of $\textbf{Na}_2\textbf{ArzH}_6$. In order to determine the stoichiometry of the complex ($\{\textbf{ArzH}_4\text{–UO}_2\}^{2-}$ or $\{\textbf{ArzH}_2\text{–(UO}_2)_2\}^{2-}$), titrations were performed in diluted acid, the ionic strength and the pH value (pH = 2.1) being fixed by precise control of the concentration of sulfuric acid ($[H_2SO_4] = 5$ mM). Figure 2b shows the absorbance measurements for titration of uranyl with $\textbf{Na}_2\textbf{ArzH}_6$. They fit well with the simulated curves obtained by assuming formation of the 1:1 complex. For a ratio $[UO_2^{2+}]_{tot}/[\textbf{Na}_2\textbf{ArzH}_6]_{tot} < 1$, the concentration of $\{\textbf{ArzH}_4\text{–UO}_2\}^{2-}$ is proportional to its absor-



Scheme 1. Structure of the 26 mono- and 25 bisphosphonate molecules considered in this works. Ⓟ = PO_3H_2.