

Evaluation of POCl₃ as a Solvent for Complexation Studies

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Mixtures of phosphorus oxychloride (POCl₃) and a Lewis acid, such as tin(IV) chloride, have been used for some time as solvents for luminescence studies of the lanthanide elements [1–5]. Solvent quenching of the lanthanide luminescence in these systems is minimal, while the salt solubilities are appreciable. These aprotic solvents have a number of properties which led us to consider their use for non-aqueous metal complexation studies. For example, phosphorous oxychloride has a wide liquid range (melting point 1.3 °C, boiling point 107.7 °C) and is optically clear in the UV–Vis range above 320 nm [1]. The specific conductivity of POCl₃ [2×10^{-8} ohm⁻¹ cm⁻¹ (20 nS cm⁻¹) at 10 °C] is on the order of that of water, and its autoionization is also similar to that of water [6]:



The addition of an aprotic Lewis acid such as tin(IV) tetrachloride serves to increase the degree of ionization of the solvent and increase the solubility of metal salts. SnCl₄ also acts as a chloride buffer to control the free chloride concentration. The 'super-acid' character of the POCl₃ + SnCl₄ solvent also suggested the possibility of interesting chemical behavior.

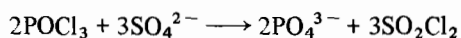
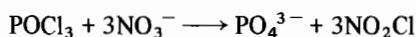
In our study, uranium in the IV and VI (*i.e.*, as UO₂²⁺) oxidation states were dissolved in the POCl₃ + SnCl₄ mixture and studied by absorption and luminescence spectroscopy and cyclic voltametry. A solvent mixture of 5 mol% SnCl₄ was used. Anhydrous UCl₄ was found to have a solubility of ~7 mM while that of anhydrous UO₂Cl₂ was ~100 mM. Figure 1 shows the visible absorption spectra of uranyl chloride and uranium tetrachloride in this solvent system. The molar absorptivities of U(VI) and U(IV) in this solvent are 3 to 5 times larger

than those in common solvents such as tributylphosphate, methanol and water [7].

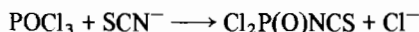
Prior research on lanthanide fluorescence lifetimes in POCl₃ indicates a large increase over that in water [1–5]. Luminescence measurements of uranyl in POCl₃:SnCl₄ solution excited at 395 nm gave lifetimes of ~200 μs. Fluorescence lifetimes of uranyl chloride in water were too short to be measured under our experimental conditions (< ~10 μs). The measured lifetimes were slightly dependent on uranyl concentration over the range of 20 to 100 mM UO₂Cl₂. At uranyl concentrations of 59 and 98 mM, a lifetime of ~280 μs was measured. At metal concentrations of 39 mM or less, the decay curve could be resolved into two lifetimes of the order of 60 μs and 300 μs. The origin of the shorter-lived species was not determined.

To evaluate the feasibility of studying complexation of uranium in POCl₃ + 5% SnCl₄, solutions of the sodium salts of acetate, sulfate, nitrate and thiocyanate were prepared. Color developed immediately in the nitrate and thiocyanate solutions and somewhat more slowly in the acetate and sulfate solutions, indicating chemical reaction between the solvent and the anions. The nitrate solution darkened from pale yellow to bright orange with time. The sulfate solution became slightly yellow as it aged, with the appearance of a shoulder in the UV spectrum of the solution. A shoulder appeared at 1800 cm⁻¹ in the IR spectrum of the acetate solution, and a second peak in the proton NMR spectrum. These spectral changes were consistent with the formation of acetic anhydride.

Phosphorus-31 spectra of the sulfate, nitrate and thiocyanate solutions were recorded as a function of time. A triplet and singlet appeared in the sulfate and nitrate solution spectra in a chemical shift region similar to that reported for phosphates. These bands were not present in the thiocyanate spectrum. The intensity of the triplet was ~1–4% of that of the POCl₃ peak which is about equivalent to the nitrate and sulfate added, indicating reaction of these anions with the POCl₃. Upon adding UCl₄ to the 'sulfate' solution, a precipitate formed. Uranium and phosphate were present in this precipitate, but sulfate was not. From these observations, we conclude that sulfate and nitrate react with POCl₃ to form phosphate, perhaps by reactions such as



Thiocyanate reacts in a different manner, perhaps by



Acetate dehydrates to acetic anhydride.

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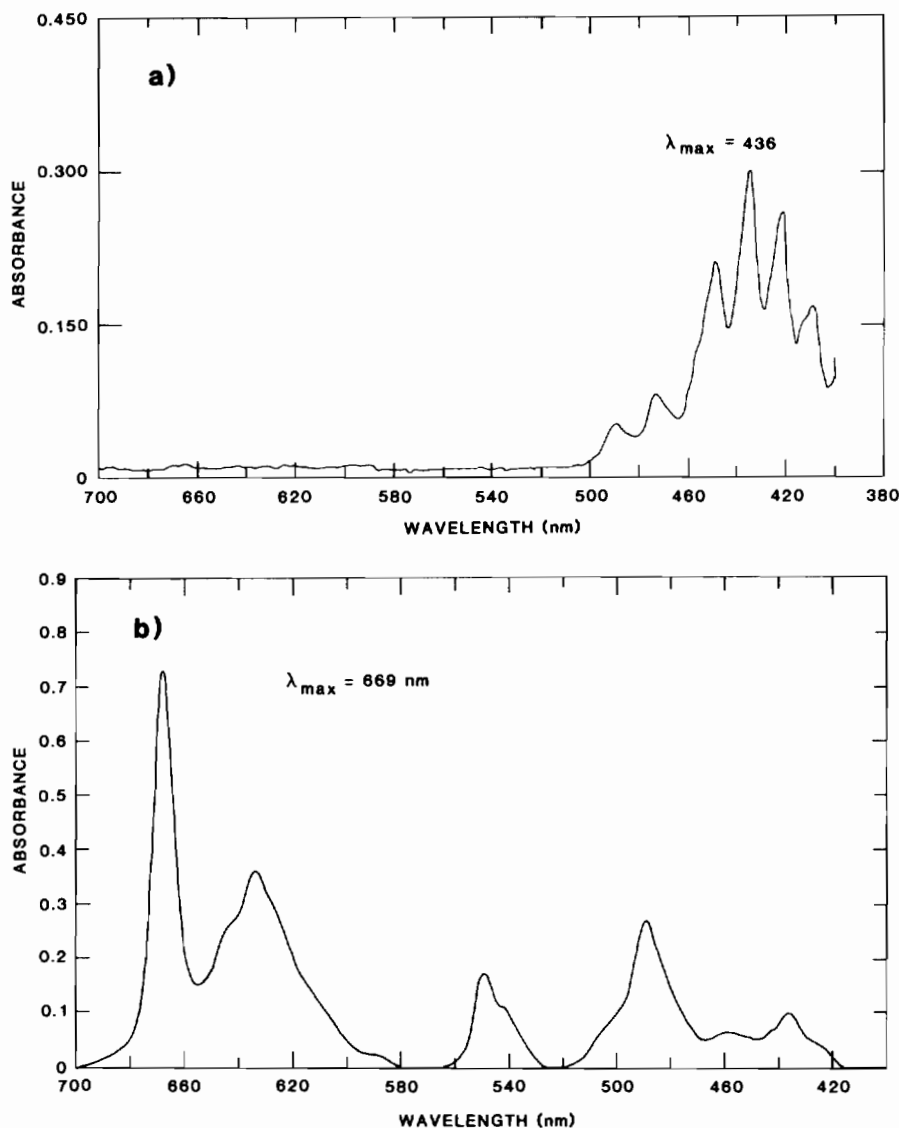


Fig. 1. UV-Vis spectra of (a) uranyl and (b) uranium(IV) solutions in $\text{POCl}_3 + 5 \text{ mol\% SnCl}_4$.

The apparent reactivity of this solvent toward common ligands made complexation studies not feasible, so our attention turned to the redox chemistry of uranium using cyclic voltametry. The highly reactive and corrosive nature of the solvent required use of platinum wire as the working, reference and auxiliary electrodes [8]. A useful potential window of approximately 1 V was obtained. Several compounds were tested as internal references*, but none was found to undergo oxidation or reduction

*Compounds tested were: ferrocene, FeCl_2 (did not dissolve), K_2MnO_4 , $\text{Ru}(\text{acac})_3$ and $\text{Fe}(\text{acac})_3$, where acac = acetylacetonate. The acac compounds were supplied by Dr K. Goldsby, Department of Chemistry, Florida State University.

within the accessible window. Replacing SnCl_4 with ZrCl_4 increased the size of the window to between 1.5 and 2.0 V and redox of an Fe(II)/(III) couple was observed. Ferrocene added to the $\text{POCl}_3:\text{ZrCl}_4$ mixture produced a solution that was initially blue-green, changing to blue in a few minutes; the intensity of the color depended on the amount of ferrocene added. The redox couple shifted about 0.5 V with the color change (Fig. 2). During the scan, reduction occurred before oxidation. This behavior is consistent with the formation of ferrocinium ion. A cyclic voltamogram of UCl_4 in $\text{POCl}_3:\text{ZrCl}_4$ solution showed no reaction within the accessible potential window. A similar solution of UO_2Cl_2 gave a measurable reduction peak, but assignment of this peak was not possible since the

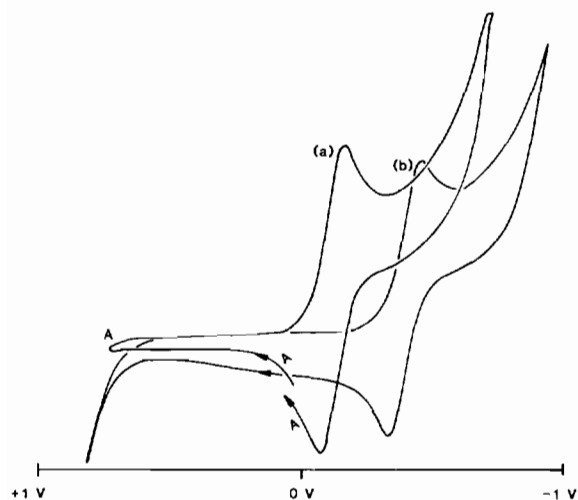


Fig. 2. Cyclic voltammograms of ferrocene in $\text{POCl}_3 + 0.35 \text{ M ZrCl}_4$ after (a) 1 min, (b) ~ 5 min.

ferrocene–ferrocinium reference couple had shifted out of the window. Attempts to find another compound useful as an internal reference were unsuccessful*.

Solvent systems of the type POCl_3 :Lewis acid appear to be too reactive for use in complexation

*Compounds tested were: $\text{Ru}(\text{acac})_3$, $[(\text{bpy})_2\text{Ru}(\text{pyc})]\text{PF}_6$ and $[(\text{bpy})_2\text{Ru}(\text{acac})]\text{PF}_6$, where acac = acetylacetonate, bpy = 2,2-bipyridine, and pyc = 2-pyridinecarboxylate. These compounds were supplied by Dr K. Goldsby, Department of Chemistry, Florida State University.

and redox studies. Organic and inorganic ligands for complexation are destroyed by the solvent, while the accessible potential window for voltametry is too narrow.

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