Sorption of Pu(IV) by Soluble Anion-Exchange Polymers

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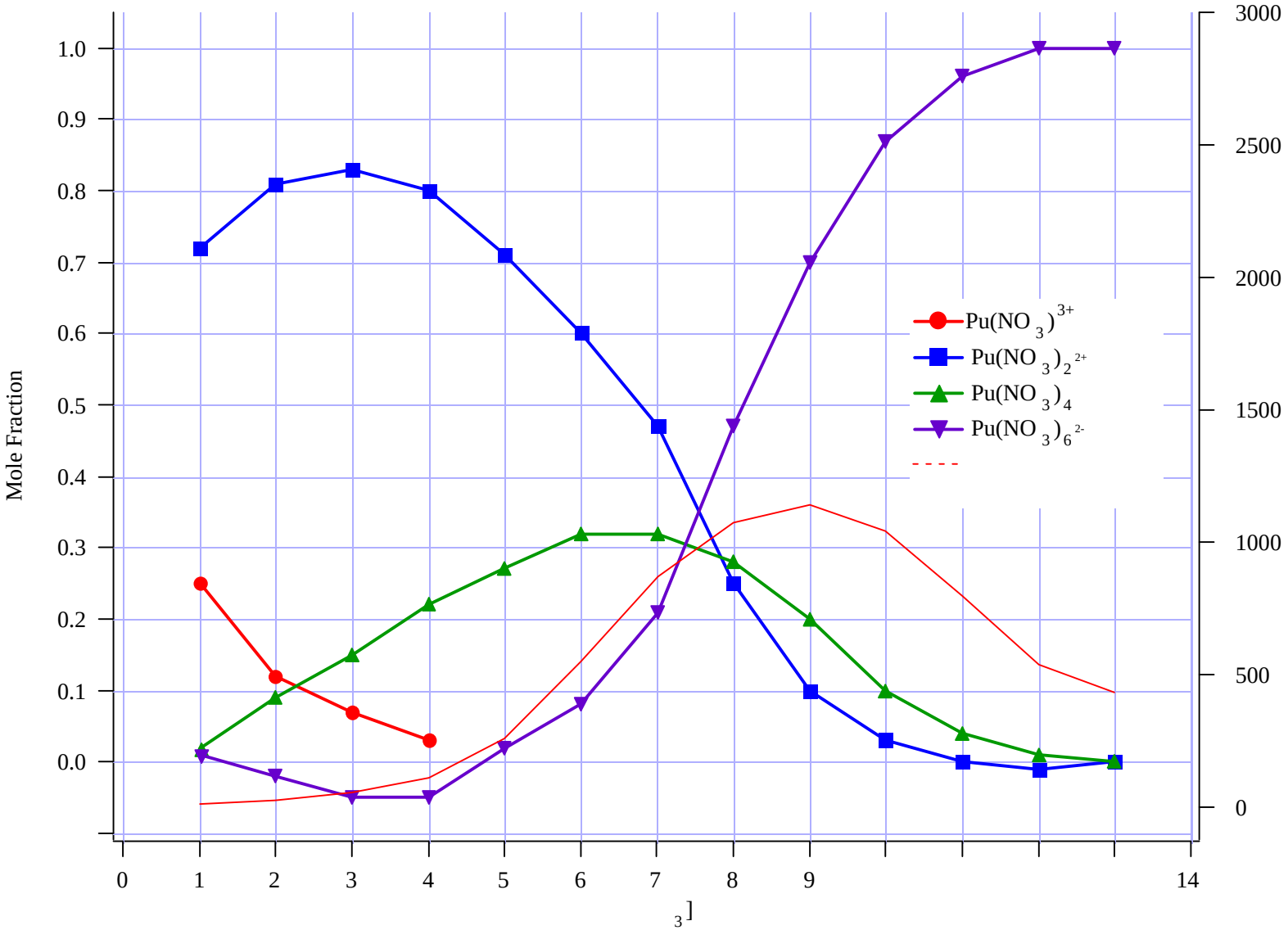
Research Objective

To develop a predictive capability for the design and implementation of selective multifunctionalized anion-exchange materials

- **Basic Scientific Issues**
  - Actinide-complex Speciation
  - Synthesis/Evaluation of New Materials
  - Molecular Modeling and Design Activities
- **EM Focus Areas/Cross-Cutting Programs**
  - Efficient Separations and Processing
  - Plutonium Plumes Mixed Wastes
  - High-Level Tank Wastes

Actinide Speciation

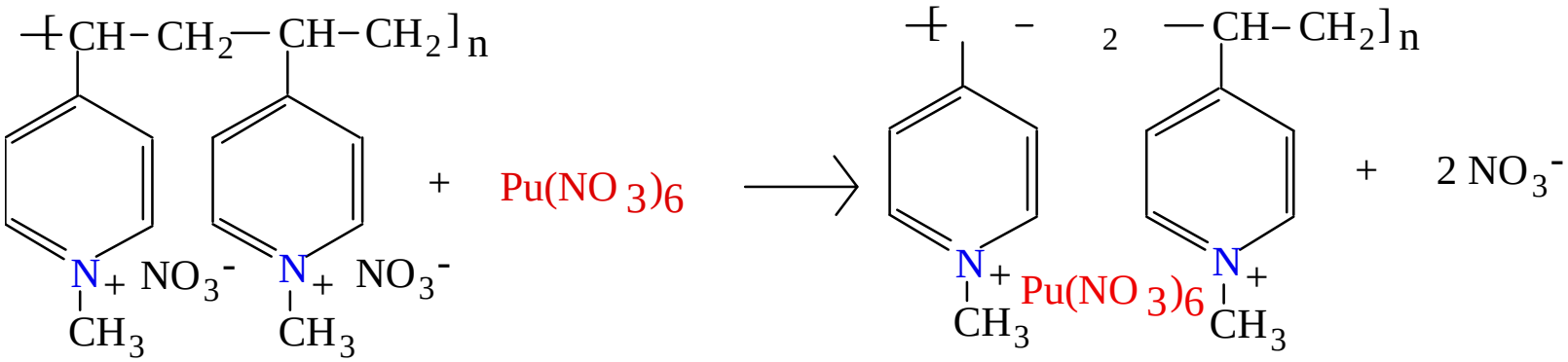


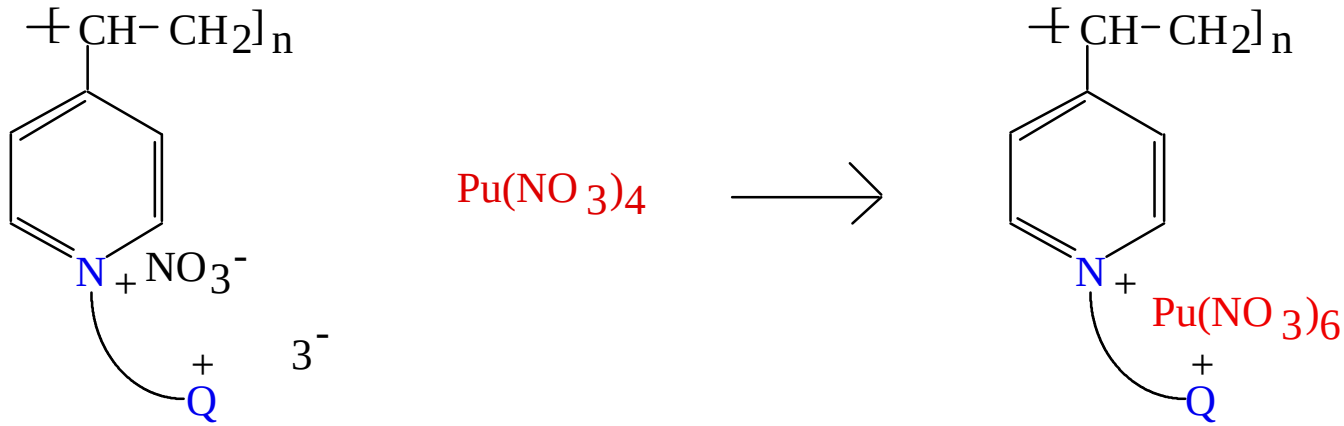
Fraction of Plutonium species vs. Nitric Acid concentration

(calculated from fit to observed visible spectral data)

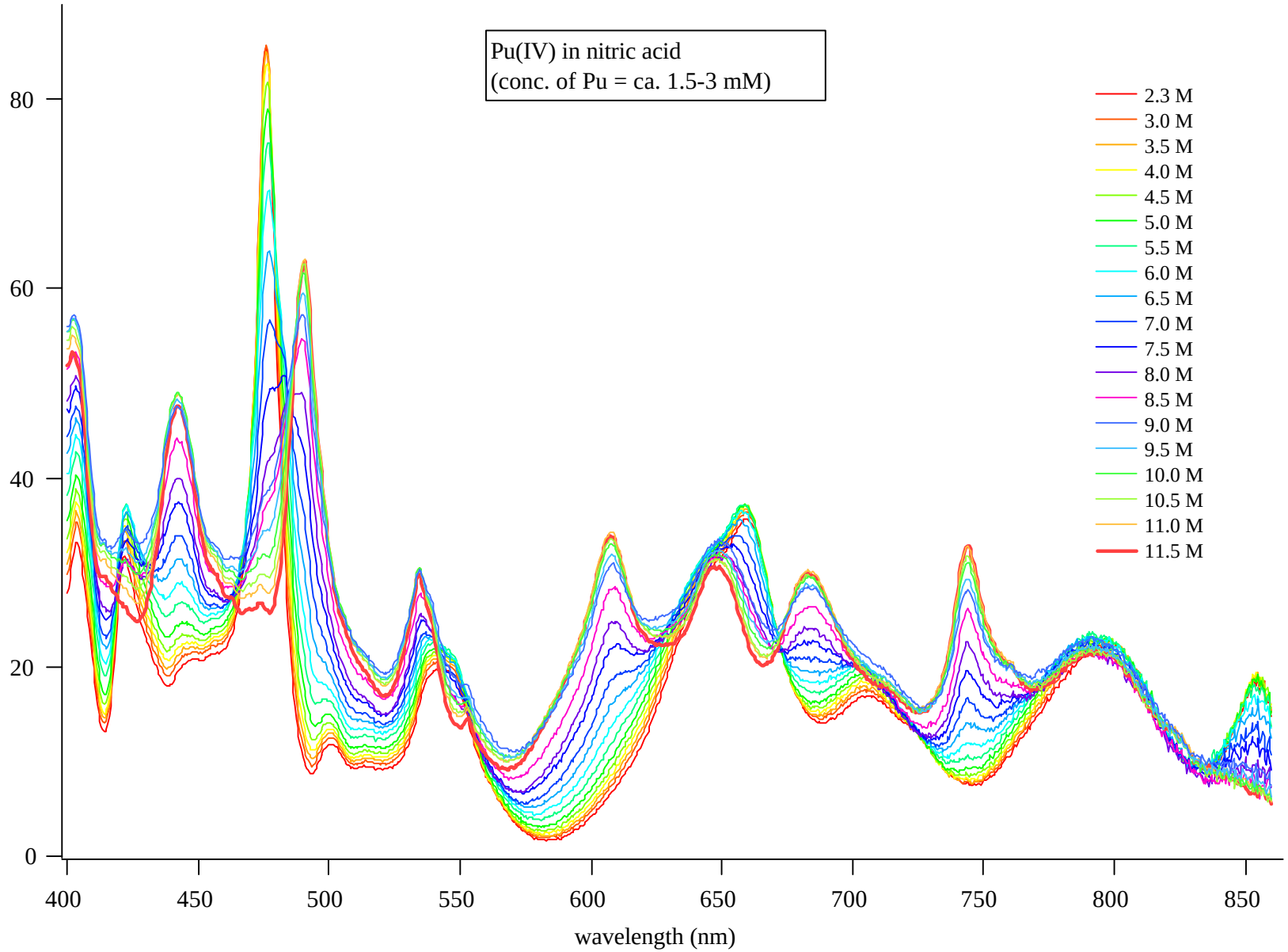
The sorption curve for plutonium onto anion-exchange resins correlates best with the solution concentration of the neutral tetranitrato complex. LA-report 12070

Conventional Uptake



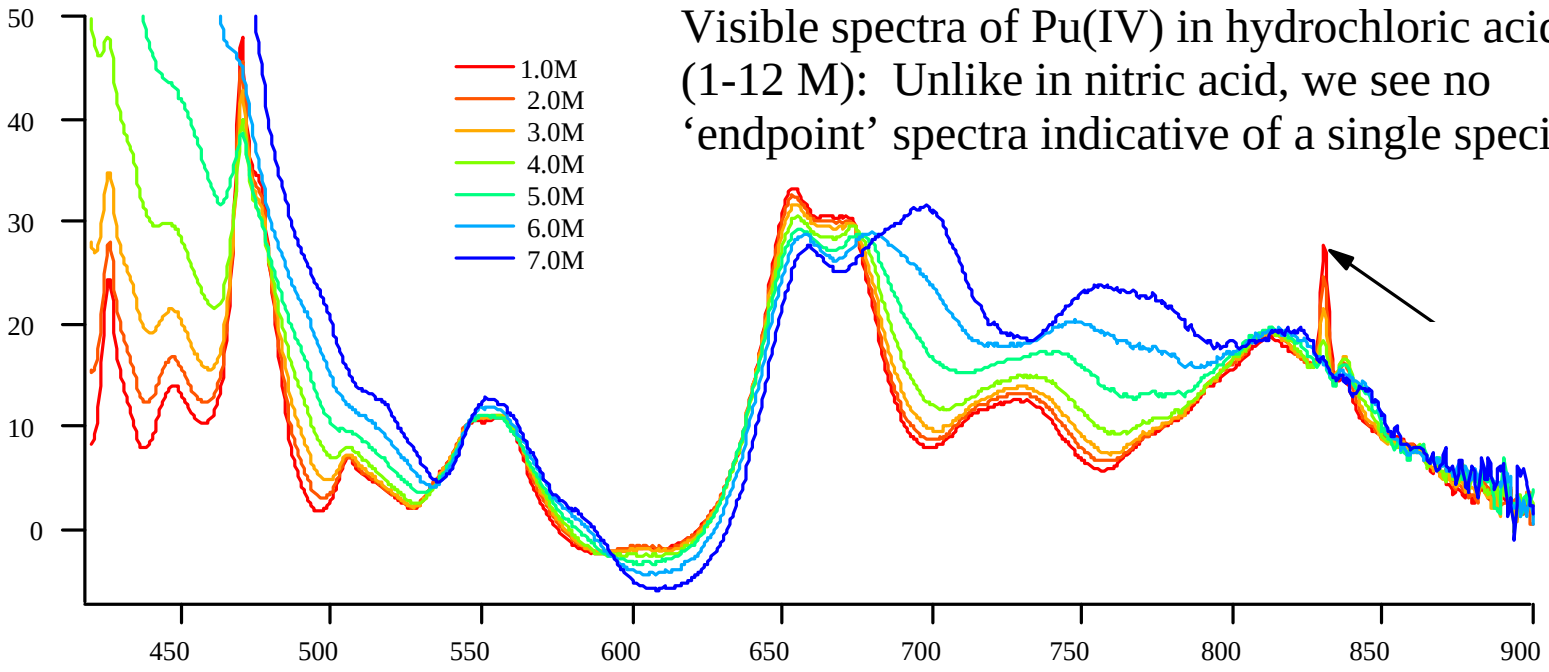


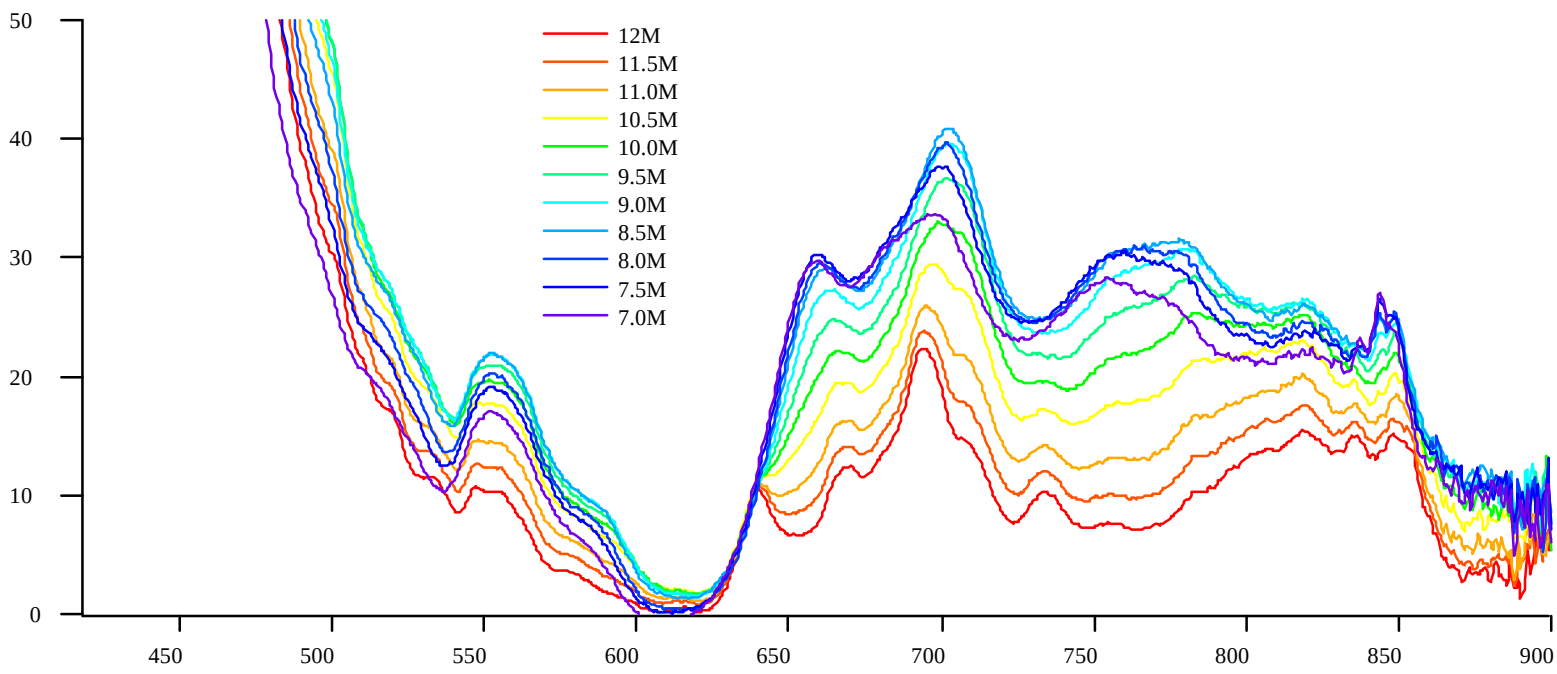
An anion-exchange site which is ‘preorganized’ to accept the tetranitrato complex could facilitate the uptake and conversion of plutonium to the bound hexanitrao complex.



The visible spectra of Pu(IV) in nitric acid reveals two ‘endpoint’ spectra associated with a single primary species: 1-3 M for the mononitrato trication and 11-14.6 M for the hexanitrato dianion. Spectra at intermediate acid concentrations are composed of multiple species.

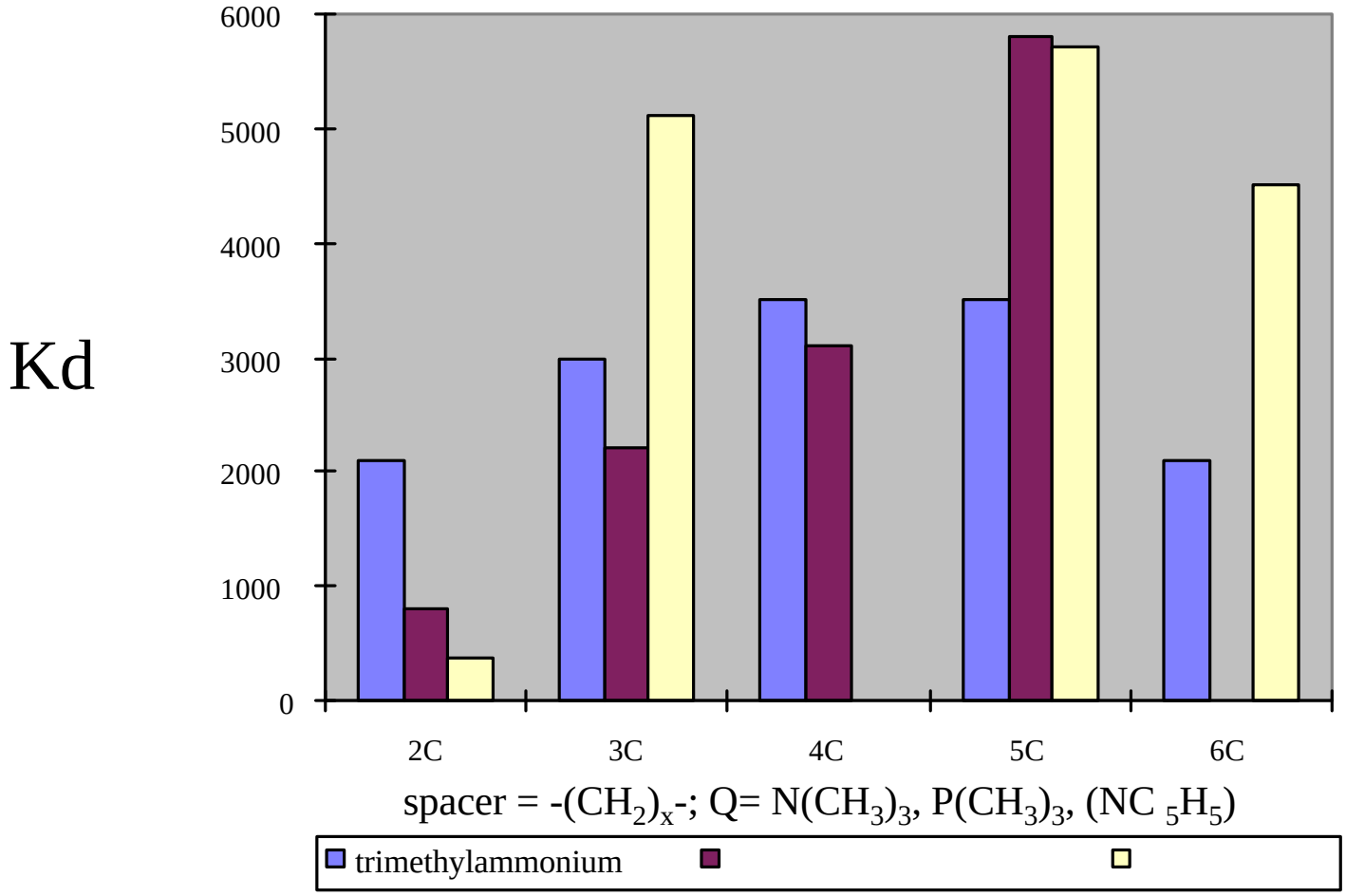
Visible spectra of Pu(IV) in hydrochloric acid (1-12 M): Unlike in nitric acid, we see no ‘endpoint’ spectra indicative of a single species.





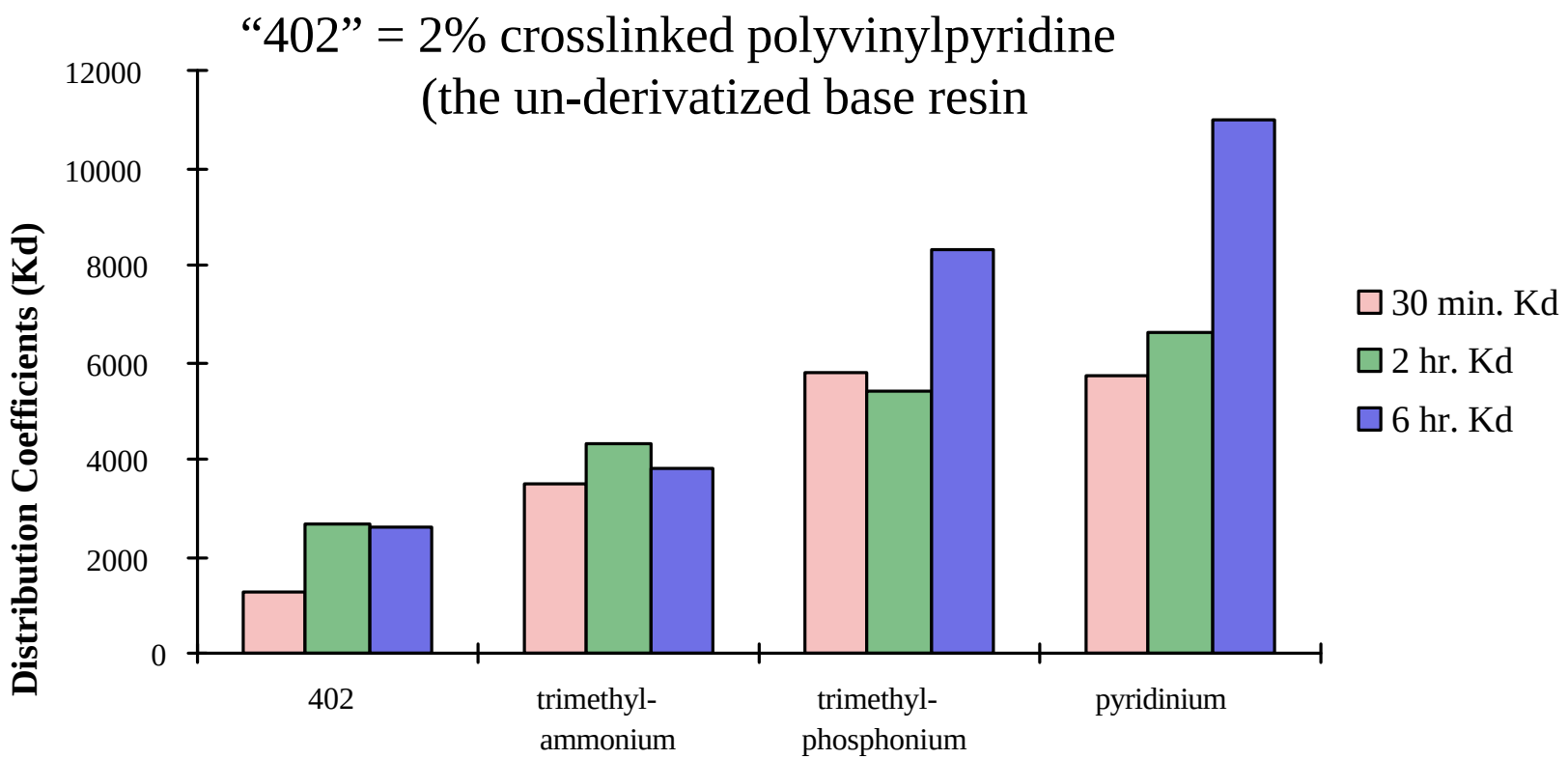
Evaluation of New Resins

30 min Kd (9M HNO_3) vs Spacer length

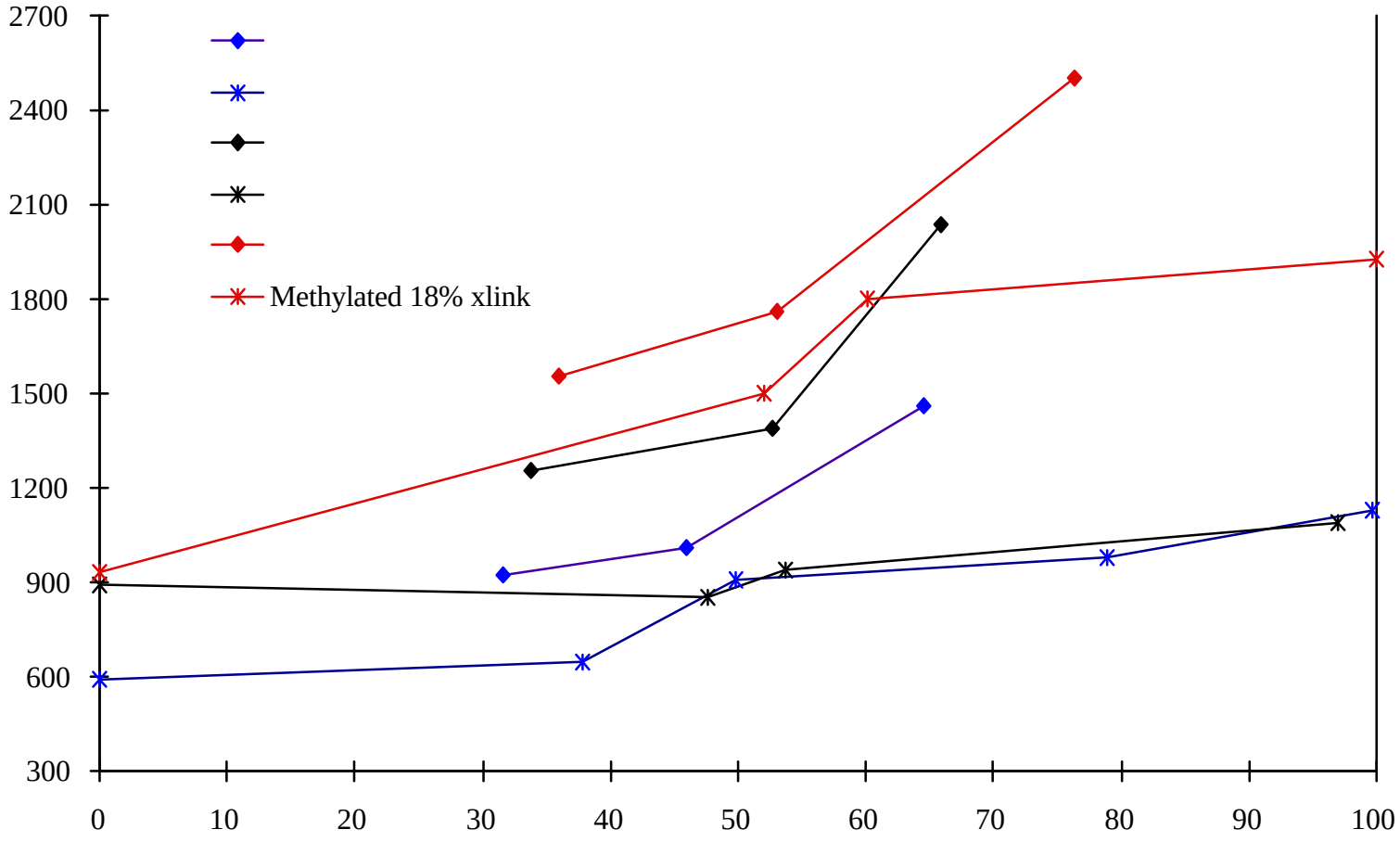


It appears tha a 4-5 methylene 'spacer' length between cationic sites is optimal for the uptake of the plutonium hexanitrato complex. We have also evaluated resin with a 5-member etherate 'spacer', $-(CH_2)_2O(CH_2)_2-N(CH_3)_3$. Resins with the etherate spacer have plutonium distribution coefficients which are up to 40% higher than for the corresponding alkylene spacer.

Kd for Pu(IV) in 7 M HNO_3 vs. Q
spacer = $-(CH_2)_5-$



The chemical structure of the second anion-exchange site (Q) has a significant impact upon the plutonium equilibrium Kd, but less impact upon the kinetics (rate) of sorption.

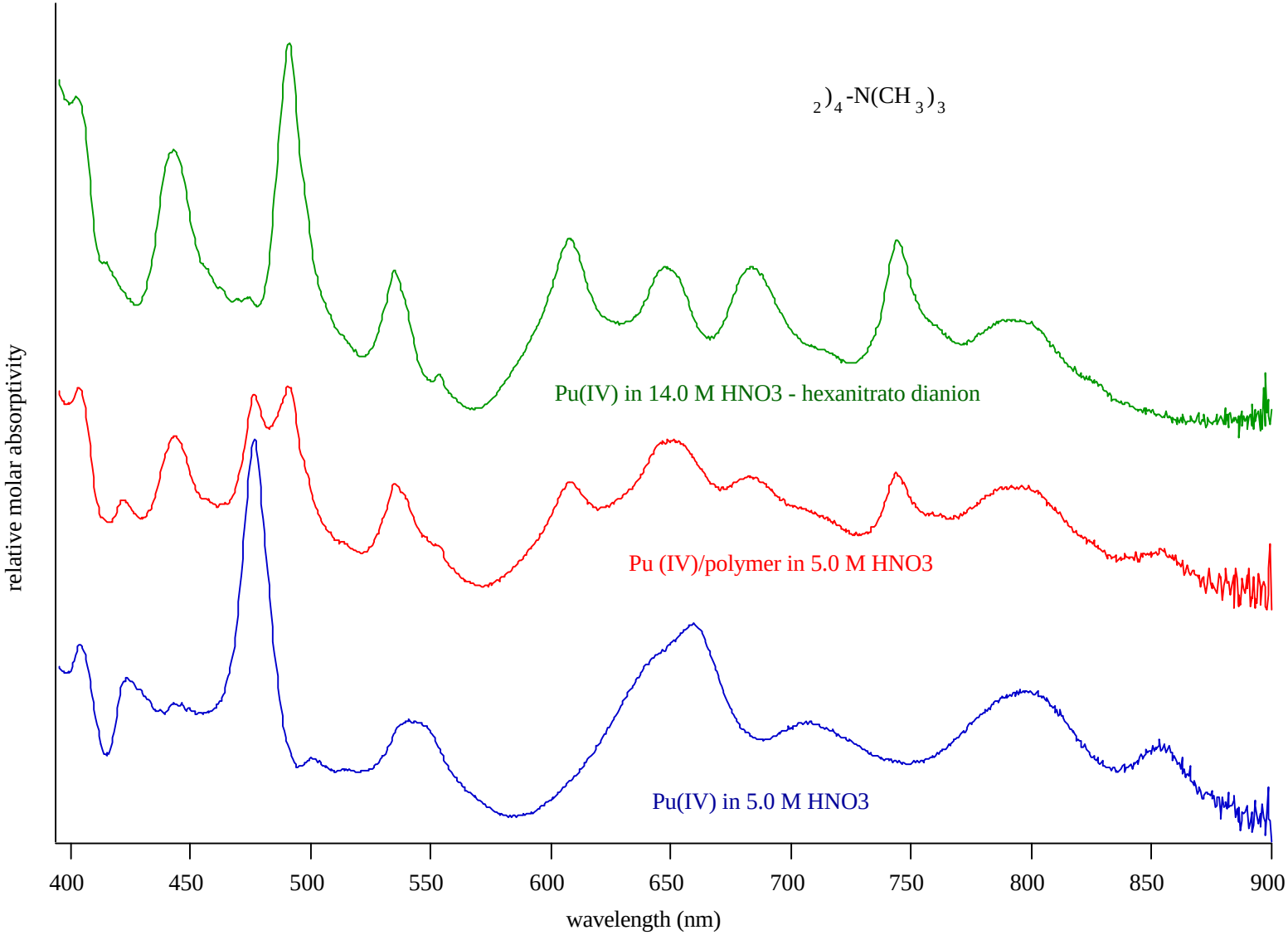


Kd vs. percent functionalization (series by % crosslinked base-resins)

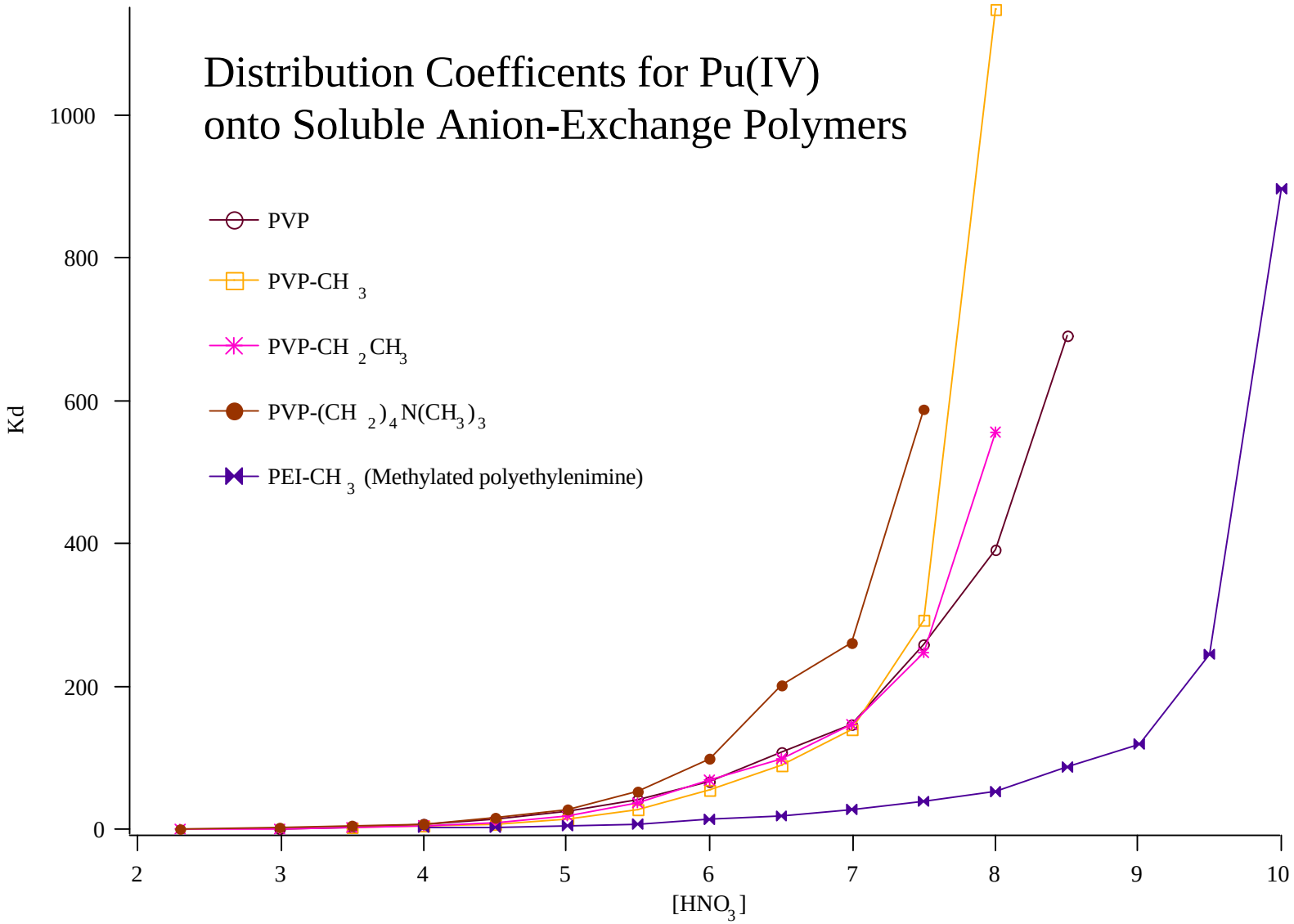
"methylated" = N-methylated polyvinylpyridine

"bifunctional" = polyvinylpyridine N-alkylated with $-(CH_2)_5N(CH_3)_3$

Distribution coefficients for plutonium from nitric acid *decrease* as the resin beads become more highly cross-linked and *increase* as a function of the number of active 'strong base' anion-exchange sites. Experimental conditions are such that Pu covers 20-25% of the active sites.



To determine the percentage of bound vs. unbound plutonium in solution with soluble anion-exchange polymers (based on linear polyvinylpyridine), we fit the spectra of Pu(IV) in the presence of the polymer to a linear combination of the spectra of Pu(IV) at the same acid concentration (% unbound) and the spectra of Pu(IV) at 14.0 M HNO_3 (% bound). In 5M HNO3, approximately 55% of the Pu is bound to the polymer.

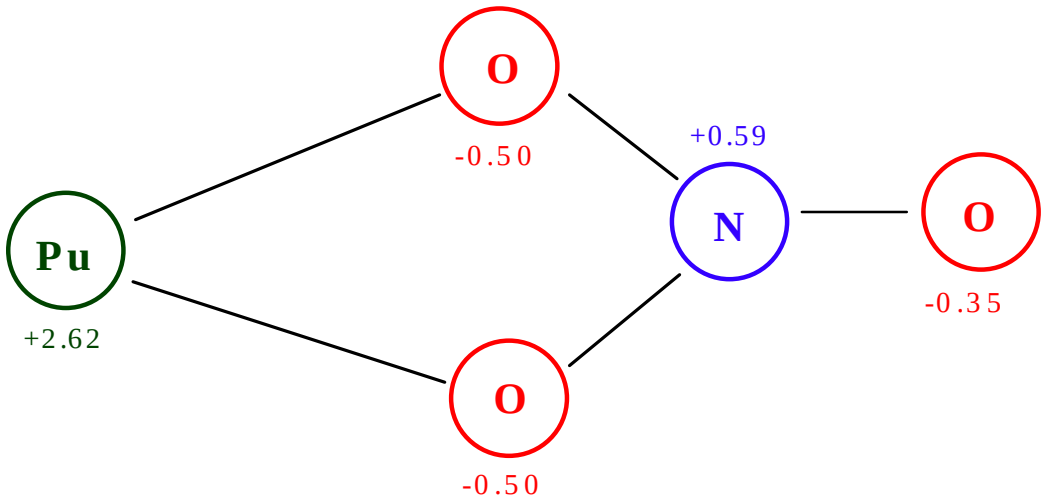


Distribution Coefficients for Pu(IV) onto the soluble anion-exchange polymers were determined using similar mass of polymer to solution volume ratios as for the solid resins. Pu-loading, however, was much lower at ca. 1 Pu per 100 cationic sites. The bifunctional polymer exhibits greater Pu affinity than the monfunctional polymers.

Molecular Modeling

Step 1: Describing the $An(NO_3)_6^{=}$ complex

- Plutonium hexanitrato partial charge distribution was estimated from ab-initio ROHF/RECP calculations on a hypothetical Pu-mononitrato tri-radical



- Bond lengths and angle were derived from EXAFS and atomic radii of the +4 actinides
- Van der Waals potential was used to describe angles and torsions
- Nitrato ligands were constrained to be planar

Step 2: Describing the Organic Dication

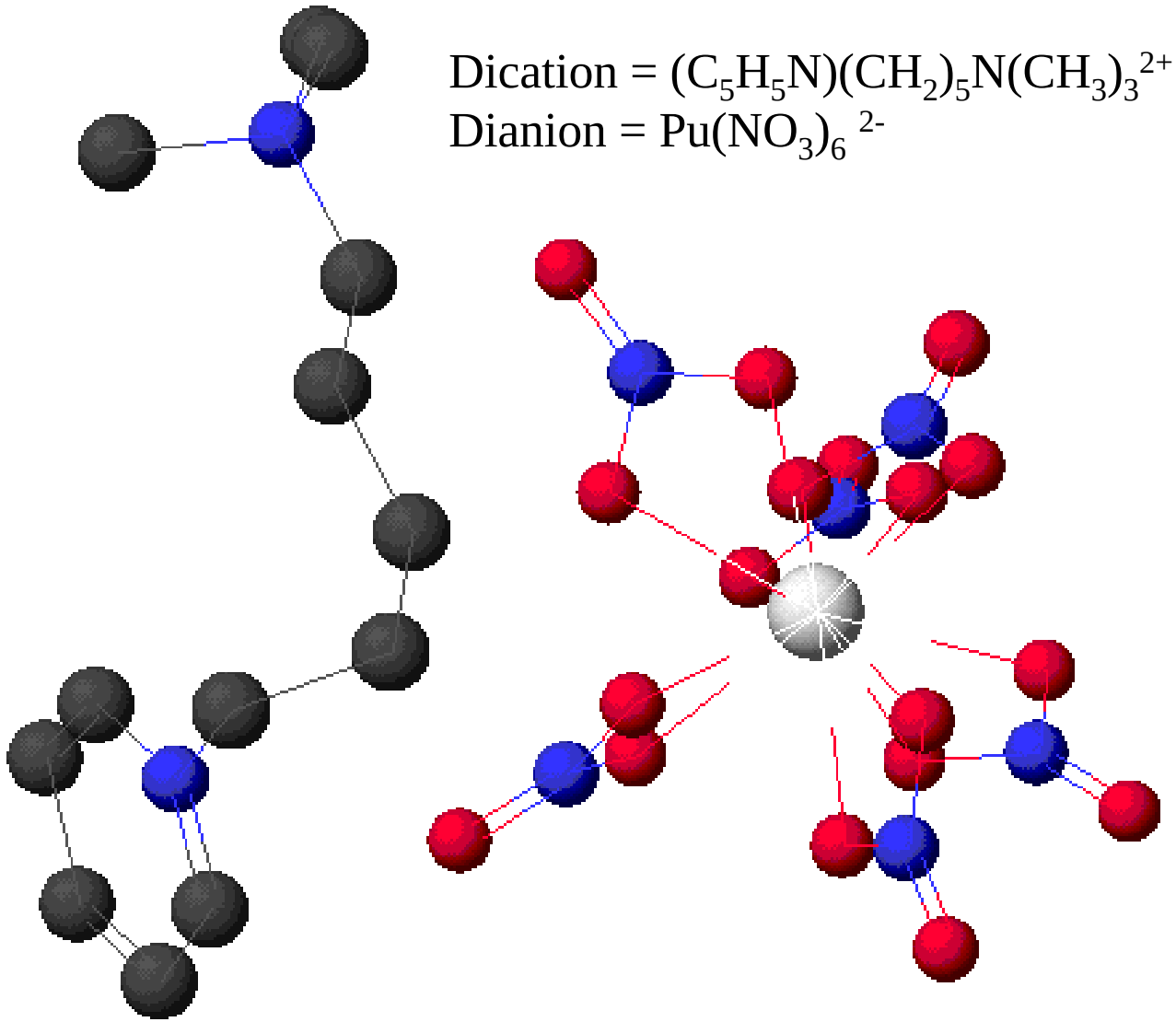
- Use the standard Allienger MM2 force field
- Replace the polyvinylpyridine resin with pyridine (‘free’ dicationic species)

Step 3: Docking the Dianion/Dication

- Try different starting configurations to find optimized ‘docked’ configurations for the dication and its interaction with the hexanitrato dianion (edge or face coordination)
- Ion pairs within 4 Å of each other will dock within 1000 iterations

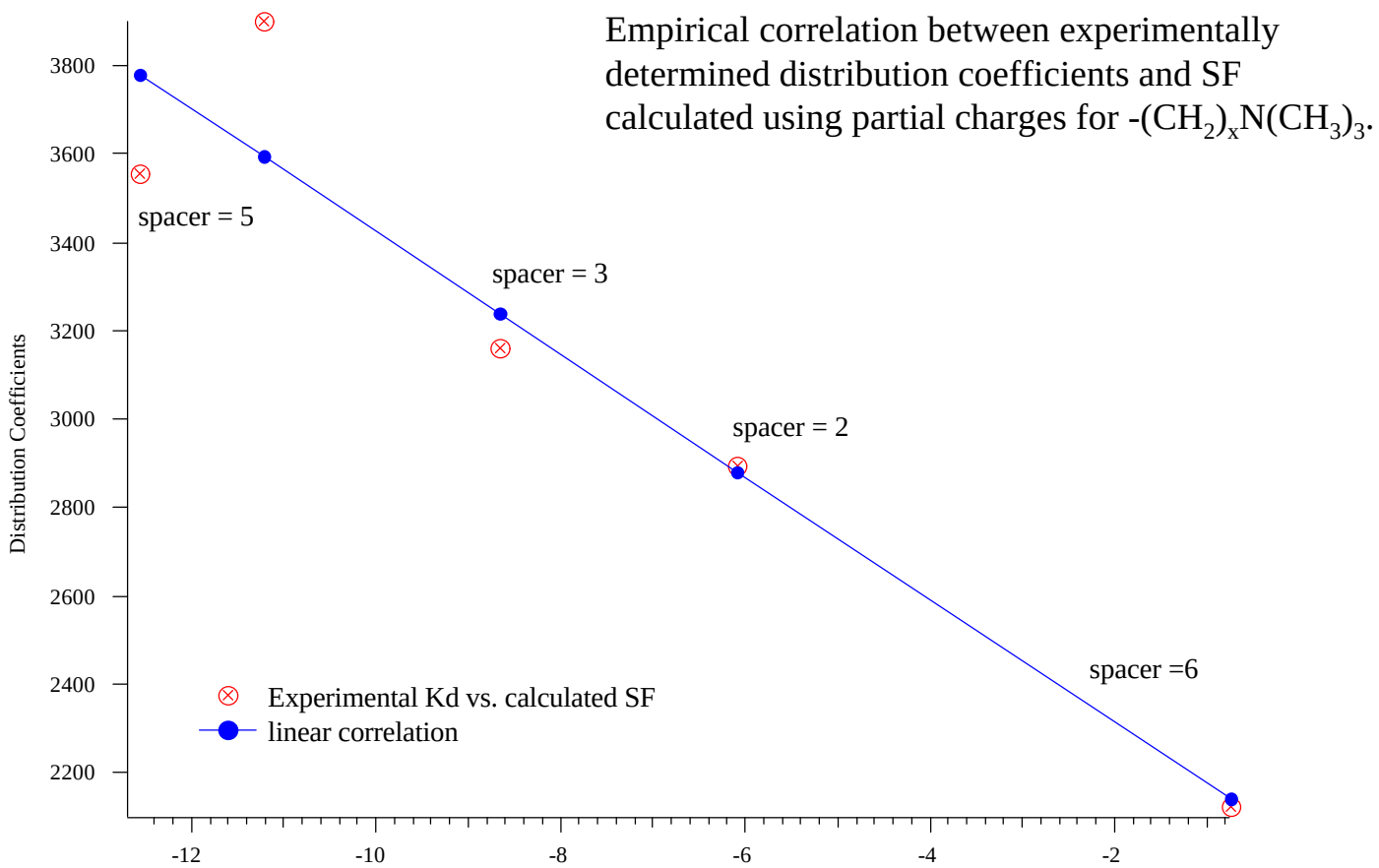
Step 3: "Docked" Model of Dication/Dianion Interaction

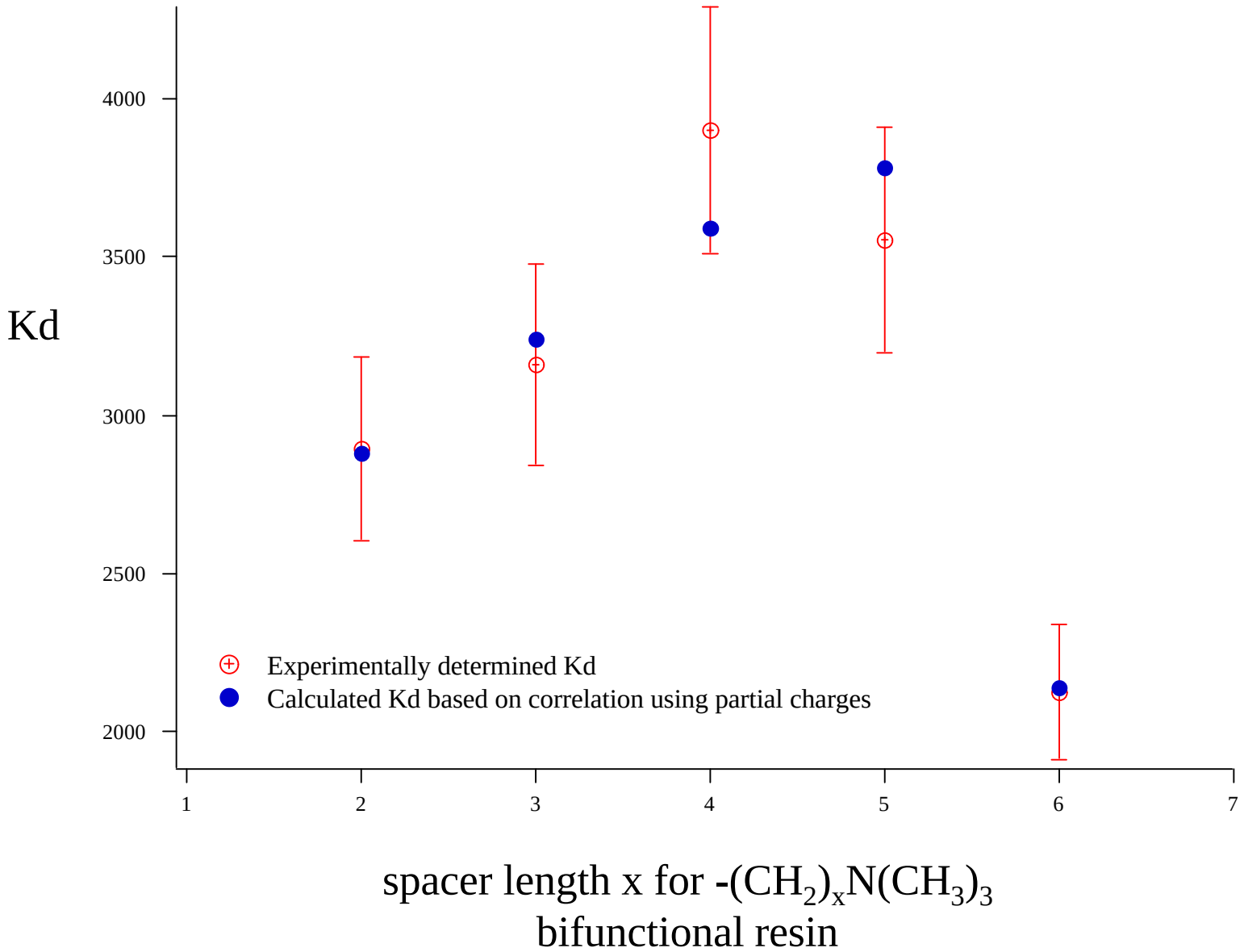
Dication = $(C_5H_5N)(CH_2)_5N(CH_3)_3^{2+}$
Dianion = $Pu(NO_3)_6^{\ 2-}$



K_d Correlation

- The Stickyness Factor (SF) is defined as the sum of the electrostatic forces
- K_d and SF are correlated by linear regression
- SF was computed using Hyperchem with either classical charges (O=-2/3, N=1, An=4,C=H=0) or calculated partial charges




Kd
4000
3500
3000
2500
2000
1
2
3
4
5
6
7
Experimentally determined Kd
Calculated Kd based on correlation using partial charges
spacer length x for -(CH2)xN(CH3)3
bifunctional resin

Summary

On-going and Future Work

- Molecular modeling of actinide complex / resin substrate interactions including solvent & resin backbone

- Synthesis and evaluation (spectroscopic/ precipitation) of corresponding 'free' dicationic pyridium derivatives

- Investigate sorption characteristics of other actinide complexes and in other media (hydrochloric acid, carbonate)

- Evaluation of corresponding dicationic pyridium extractants

- Systematically isolate energy terms of variables
  - functional group
  - spacer length
  - spacer characteristics
  - percent functionalization
  - percent cross-linking of base and final resins

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Key Contributors

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Note

All resin structures discussed in this talk (and some others not discussed) are covered by a Los Alamos National Laboratory Patent (pending).