New Anion-Exchange Resins for Improved Separations of Nuclear Materials

EMSP FY97-00

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Research Objective

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

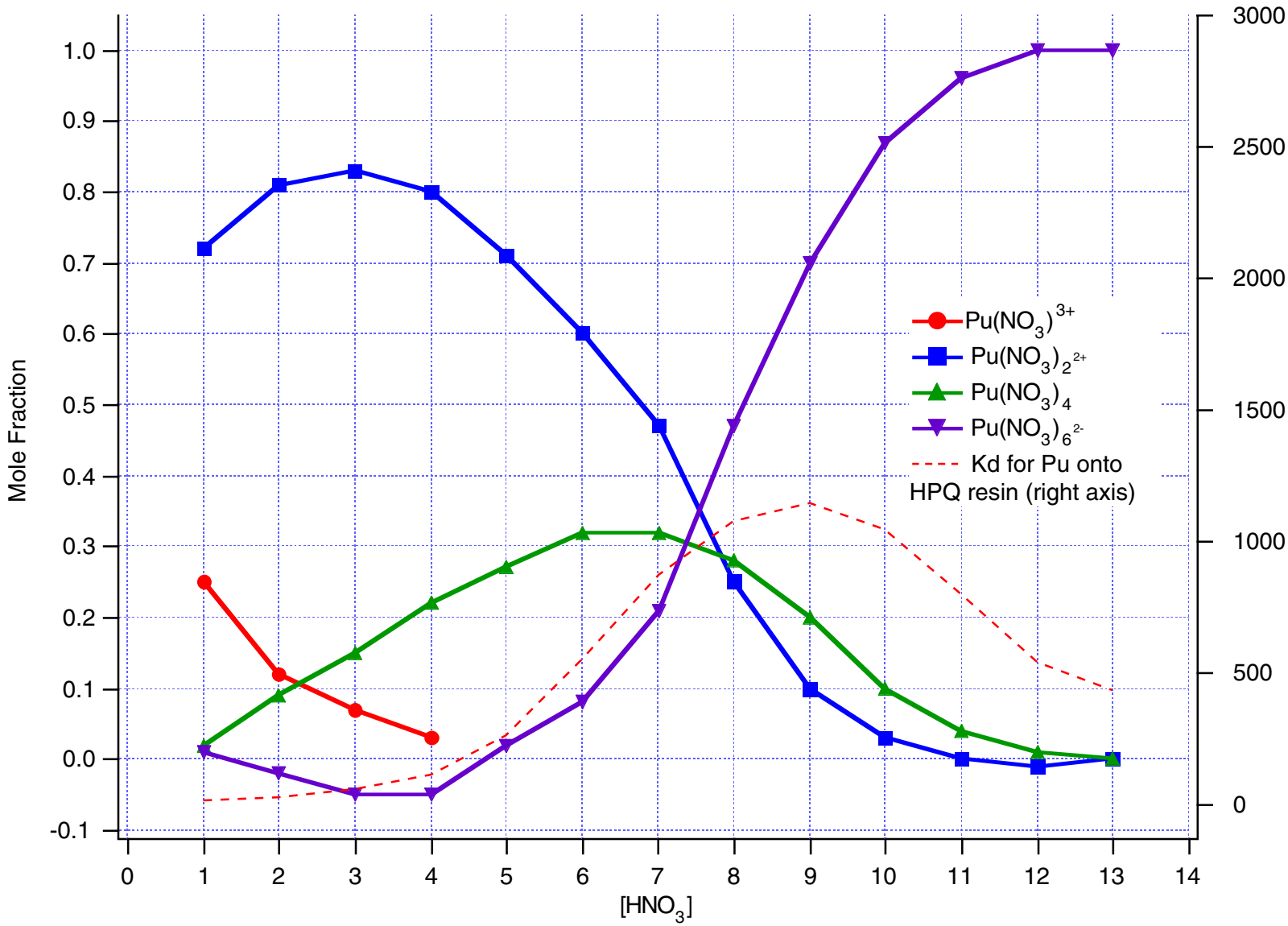
- **Basic Scientific Issues**
  - Actinide-complex speciation
  - Synthesis/Evaluation of New Materials
  - Molecular modeling and design activities

- **EM Focus Areas and Cross-Cutting Programs**
  - Efficient Separations Tanks
  - Plutonium Mixed Wastes
  - Subsurface Contaminants

DOE Separation Technology Challenges

- U.S. DOE faces many challenges in the 21st Century that require advances in separation technology
  - continuing missions require purification and processing of radioactive materials with increased safety, reduced wastes and emissions
  - cleaning up the legacy of over 50 years of production operations including aiding efforts in the former Soviet Union
  - major improvements in the nuclear power fuel cycle are possible with new approaches to separating irradiated fuel components
- Teaming with industry to develop new technology often requires markets larger than DOE operations provide

Actinide Speciation

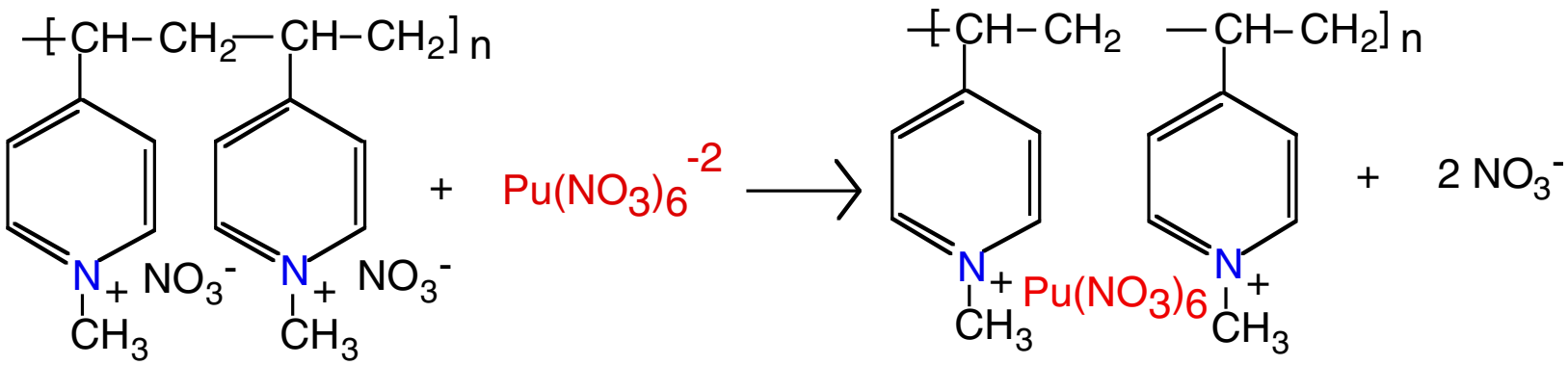


Fraction of Plutonium species vs. Nitric Acid concentration

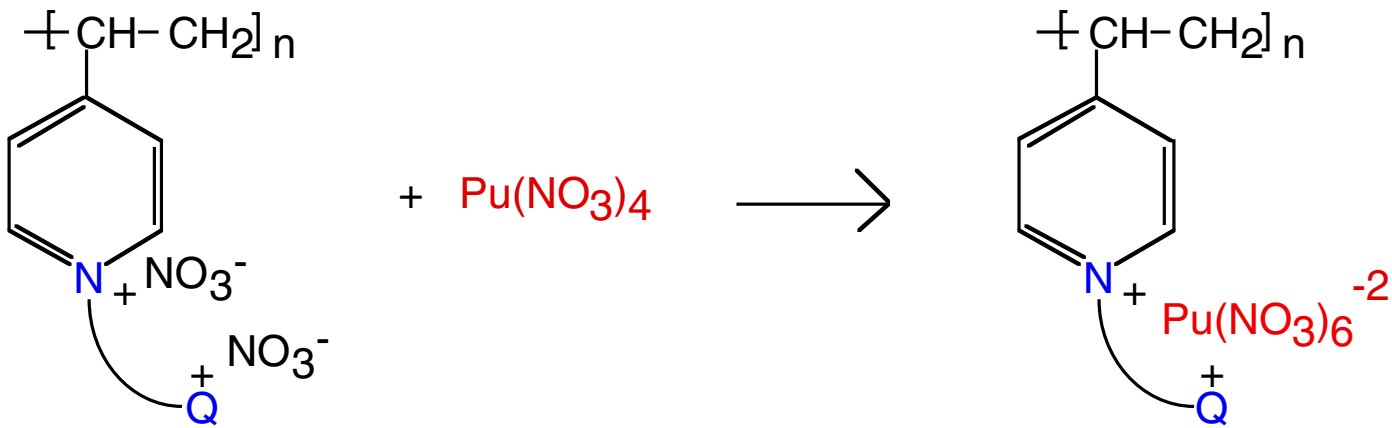
(calculated from fit to observed visible spectral data)

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

Conventional Uptake

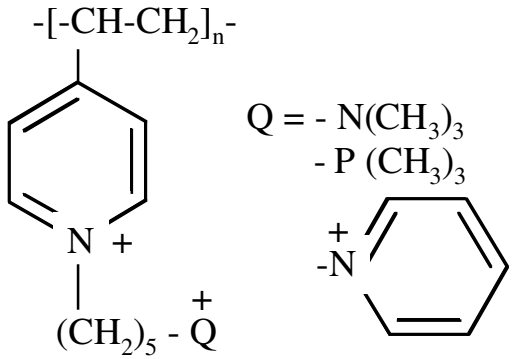


"Facilitated Uptake"

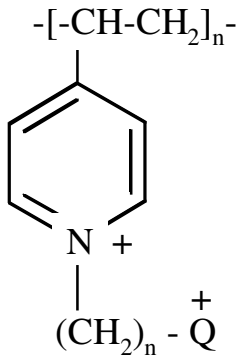


An anion-exchange site which is ‘preorganized’ to accept the tetranitrato complex could facilitate the uptake and conversion of plutonium to the bound hexanitrao complex.

Evaluation of New Resins

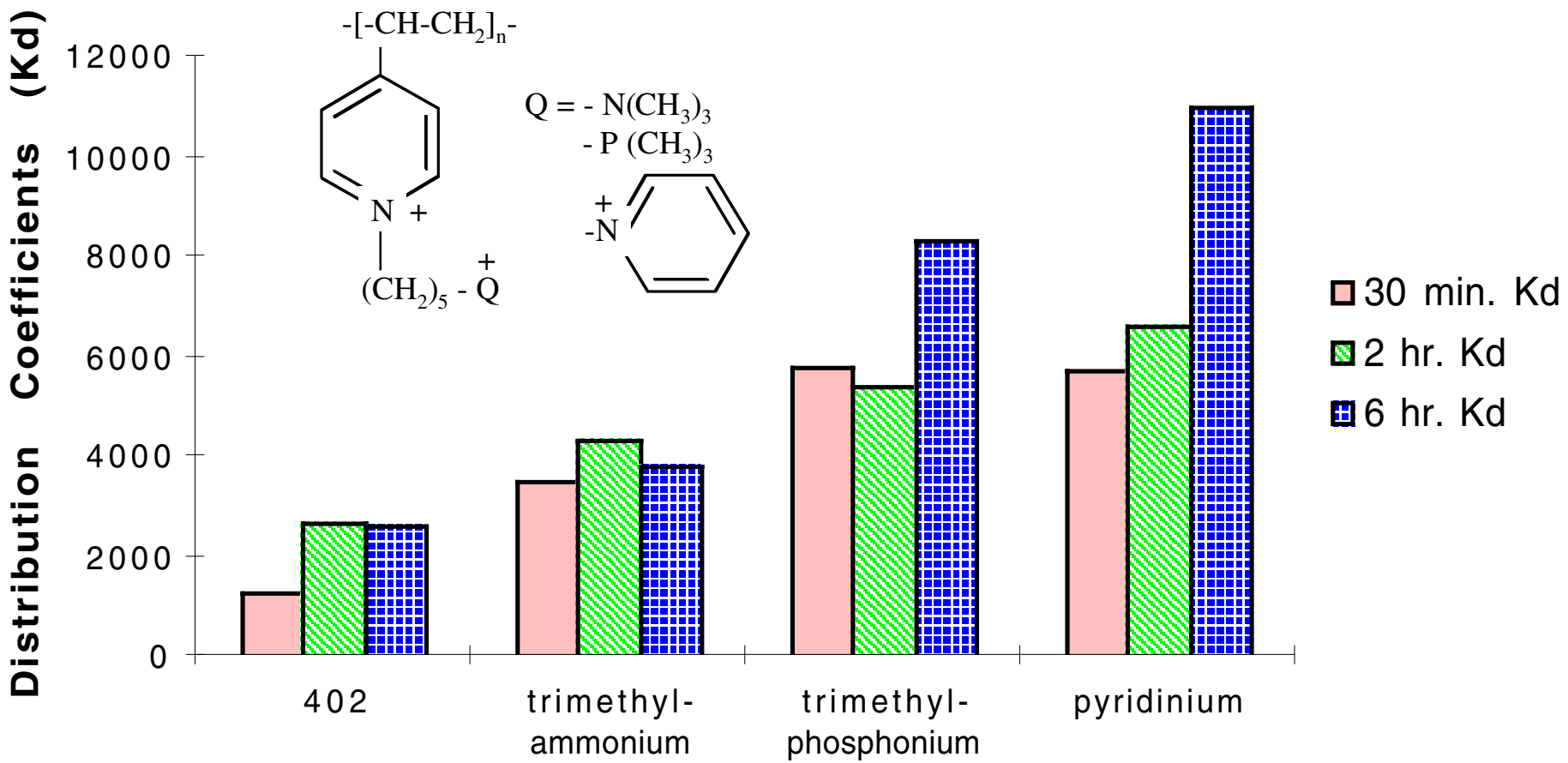


Q = - $N(CH_3)_3$
- $P(CH_3)_3$



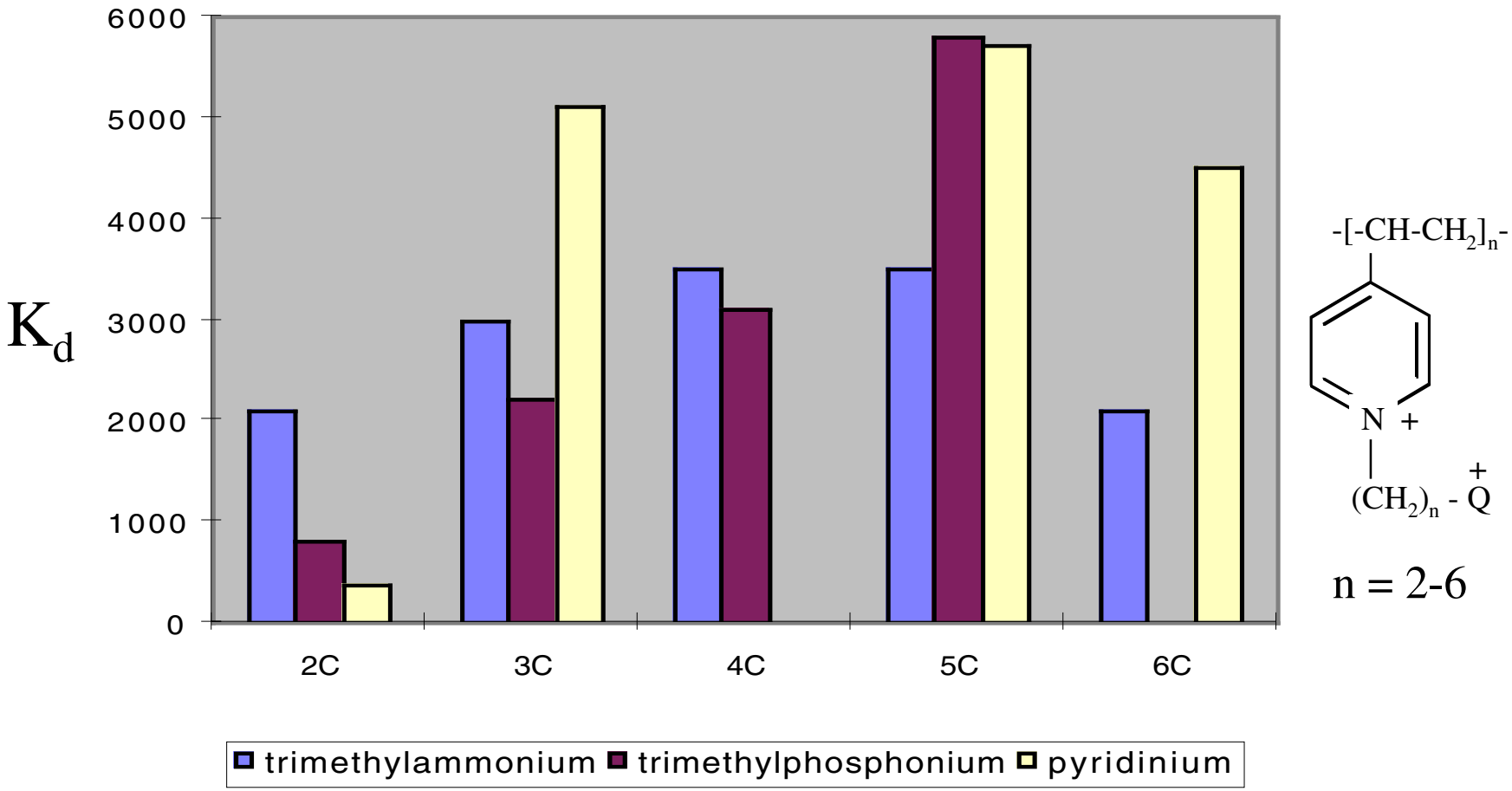
n = 2-6

K_d for Pu(IV) in 7 M HNO_3 vs. Q

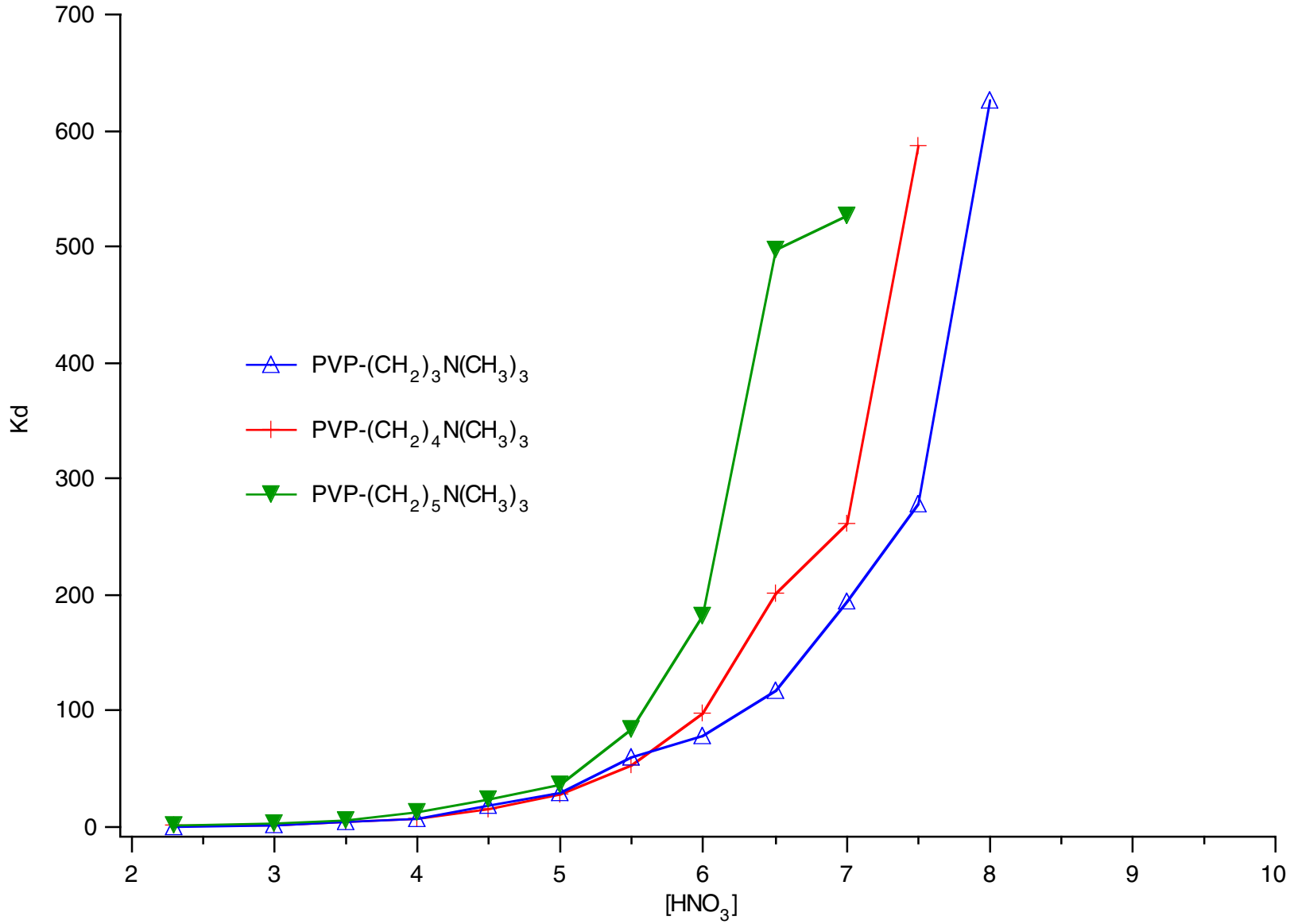


The chemical structure of the second anion-exchange site (Q) has a significant impact upon the plutonium equilibrium K_d, but less impact upon the kinetics (rate) of sorption.

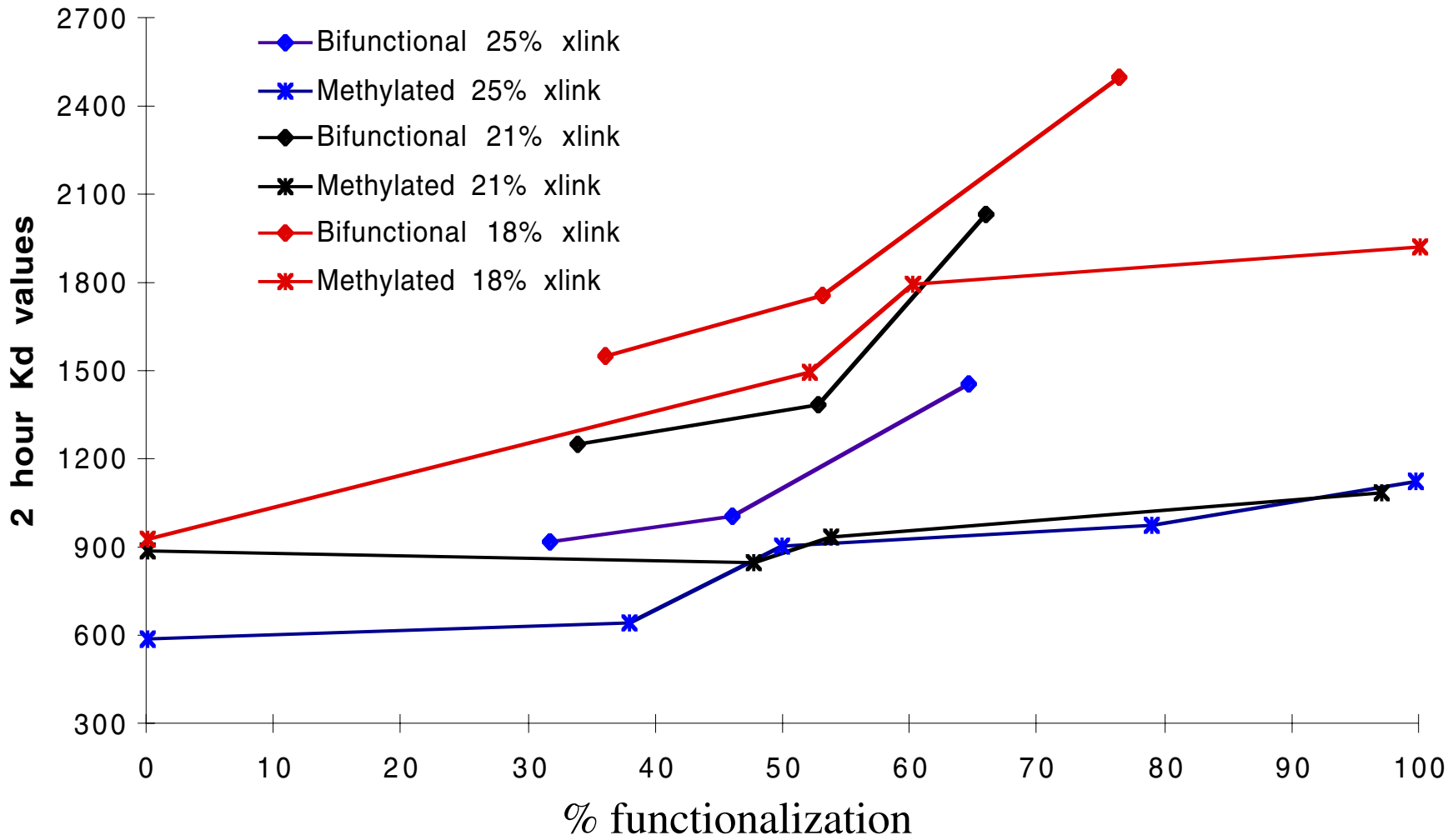
30 min K_d (9M HNO_3) vs Spacer Length



Plutonium distribution coefficients maximize at a 4-5 methylene 'spacer' length between cationic sites. We have also evaluated resins 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.


700
600
500
400
300
200
100
0
Kd
PVP-(CH2)3N(CH3)3
PVP-(CH2)4N(CH3)3
PVP-(CH2)5N(CH3)3
2
3
4
5
6
7
8
9
10
[HNO3]

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

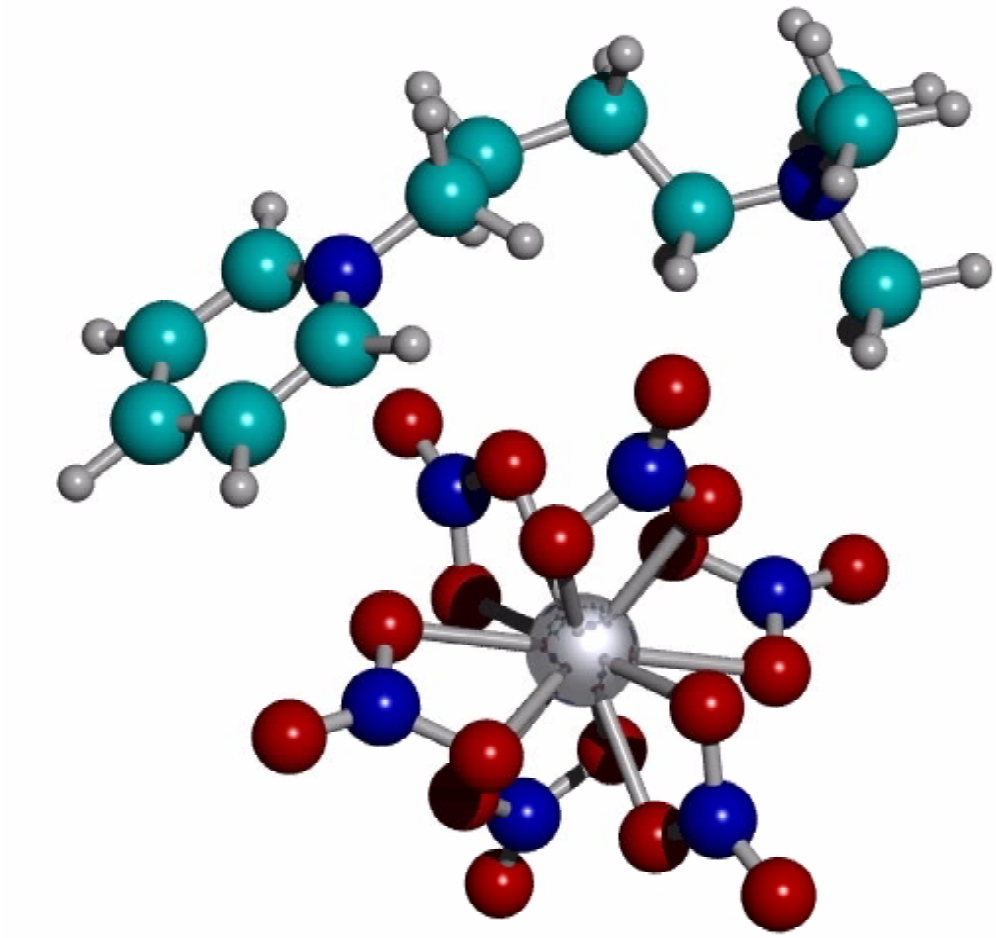


"methylated" = N-methylated polyvinylpyridine

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

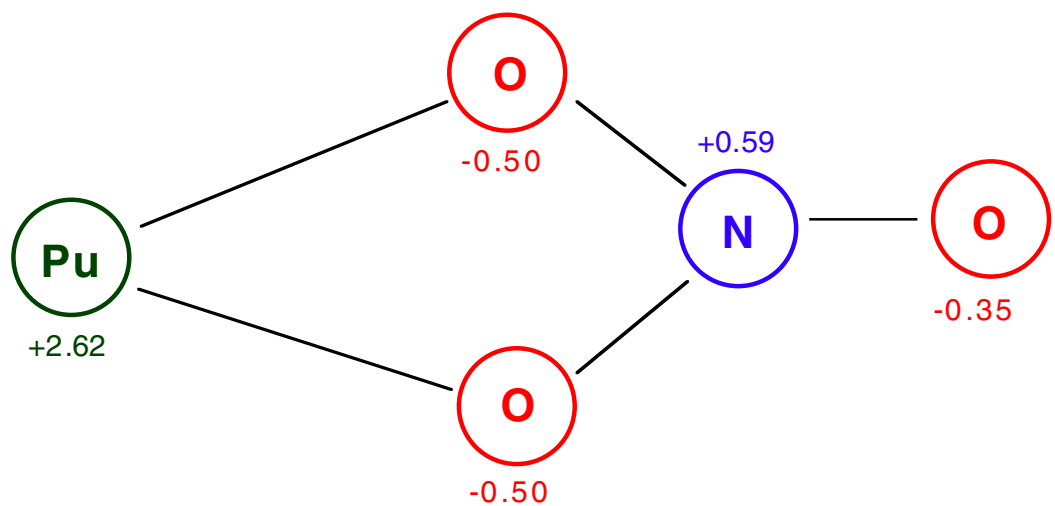
Molecular Modeling

Model of $Pu(NO_3)_6^{-2}$ 'docked' with PVP-$(CH_2)_4$-NMe_3



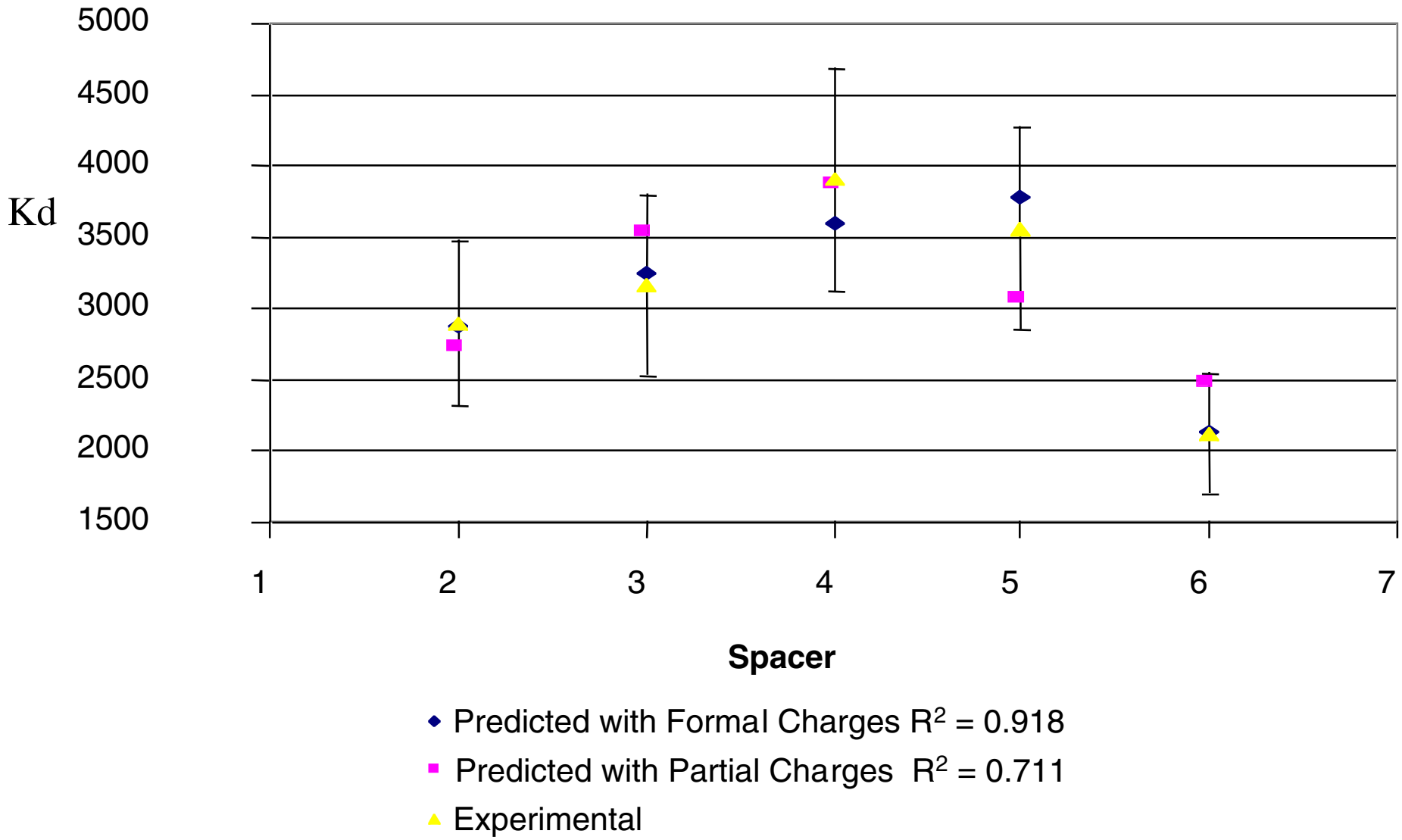
Describing the $An(NO_3)_6^{=}$ complex

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



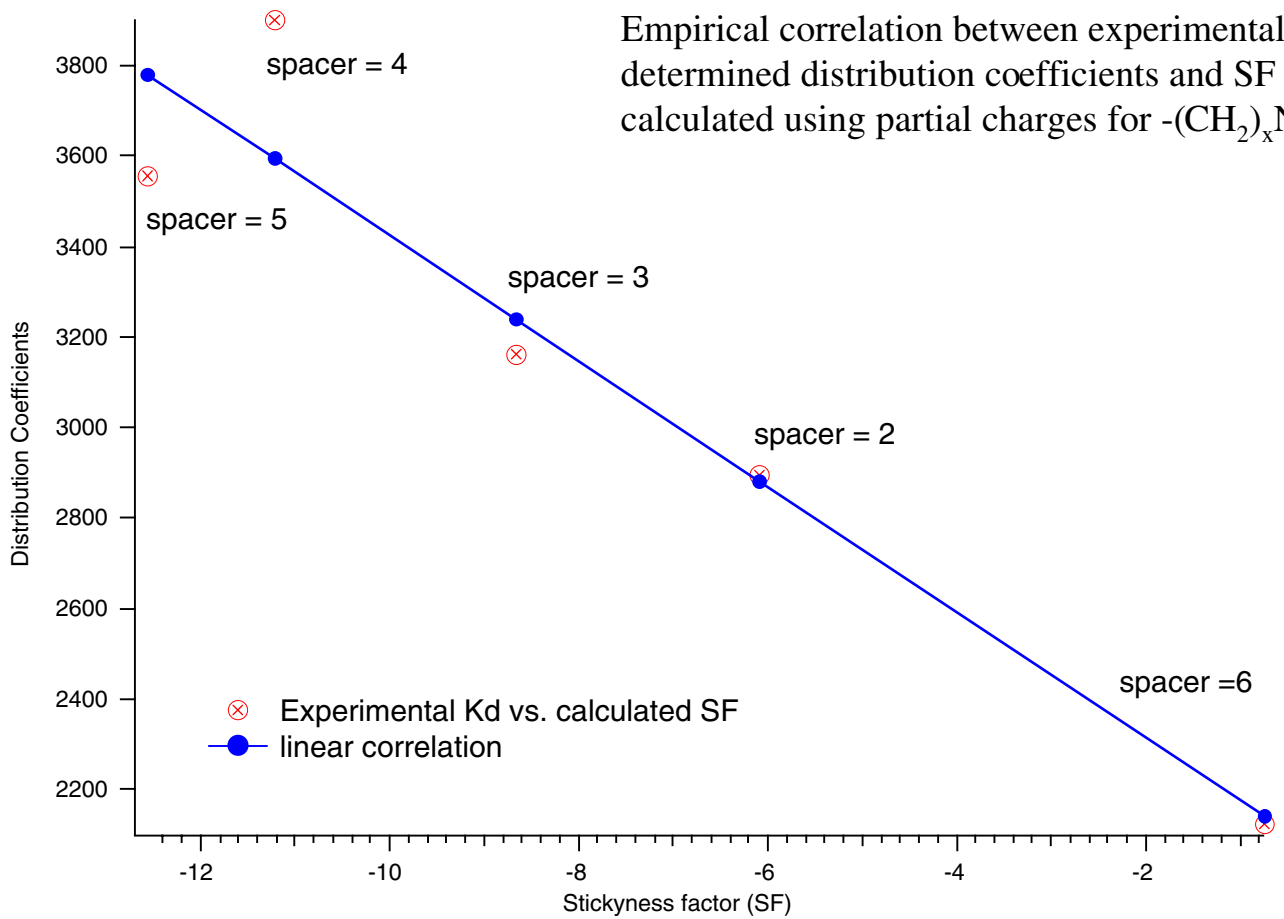
- Van der Waals potentials were used to optimize angles and torsions

$C_5H_5N(CH_2)_xN(Me)_3$



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



Empirical correlation between experimentally determined distribution coefficients and SF calculated using partial charges for $-(CH_2)_xN(CH_3)_3$.

Alpha Activity Removal

Alpha Activity Removal from Pu Processing Wastes

Programmatic Driver

To produce WIPP-certifiable cemented waste

Problem

Current cemented drums exceed the Decay Heats loading limits by 2-4X

Goals

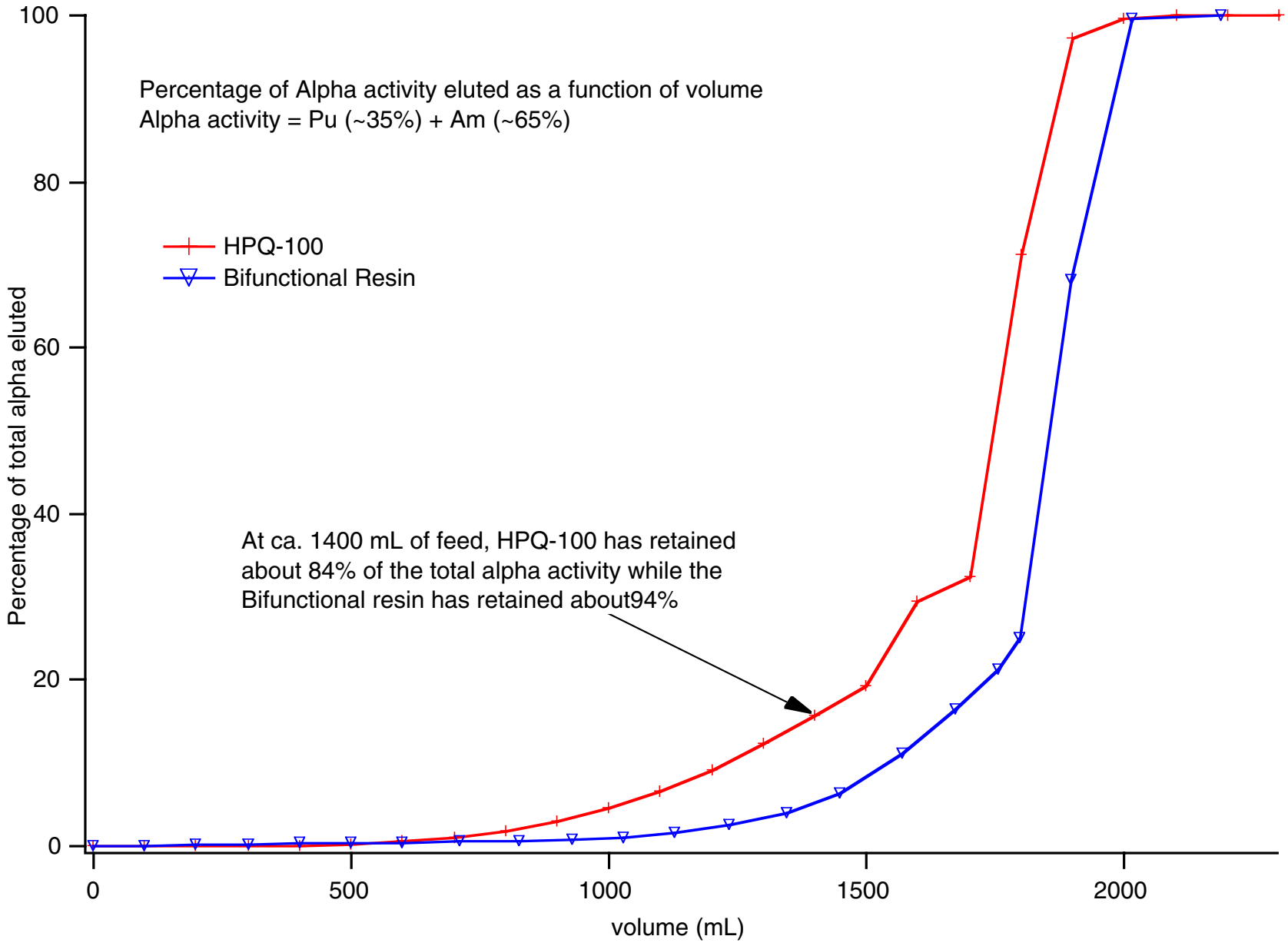
To reduce Am content of evaporator bottoms to less than 0.03 g/L of bottoms or 1.5 g/drum

"Oxalate #2" (~ 1 M H^+)

init. activity = 1.44 x 10^9 dpm/mL
~0.129 g/L Am (~64% a activity)
~2.95 g/L Pu (~36% a activity)
contact 100 mg w/ 2.5 mL, 1st contact 6 hrs, 2nd overnight

Percentage of α activity removed

	1st	2nd	total
TRU-Spec	34	12	42
HPQ (100)	61	73	90
HP-18	64	72	90
(18% xlinked, methylated, Reilly Industries)			
SE-27	67	82	94
(25% xlinked bifunctional, $-(CH_2)_5-N(CH_3)_3$)			


Percentage of Alpha activity eluted as a function of volume
Alpha activity = Pu (~35%) + Am (~65%)
HPQ-100
Bifunctional Resin
At ca. 1400 mL of feed, HPQ-100 has retained about 84% of the total alpha activity while the Bifunctional resin has retained about94%
Percentage of total alpha eluted
volume (mL)
0
20
40
60
80
100
0
500
1000
1500
2000

Ongoing and Future Work

- Evaluation of extraction properties of analogous bifunctional reagents in organic solvents
- Complete investigation of resin sorption characteristics for actinides in other media, e.g., U(VI) in carbonate
- Calorimetric measurements of ion exchange equilibria with water-soluble polymers and resins
- Molecular modeling of interactions of anionic metal complexes with polymer ion exchange sites including solvent and more extended organic structure

Conclusions

Bifunctional anion-exchange resins enhance the efficiency with which Pu(IV) can be removed from 7-9 M nitric acid.

Structural variation within the bifunctional anion-exchange resin influences the Pu(IV) sorption ability.

Molecular modeling of interactions of anionic metal complexes with bifunctional anion-exchange resins correlates with the experimental results.

Bifunctional anion-exchange resins effectively reduce alpha activity from solutions containing Pu and Am.

Contributors

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Note: Some resin structures discussed in this talk are covered by a Los Alamos National Laboratory Patent

Publications

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment" Marsh, S. F.; Jarvinen, G. D.; Bartsch, R. A. *Reactive Polymers* 1997, *35*, 75-80.

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment-II" Marsh, S. F.; Jarvinen, G. D.; Bartsch, R. A.; Nam, J.; Barr, M. E. *J. Radioanal. Nucl. Chem.* , 1998, *235*, 37-40.

Planned Publications

"Extension of Molecular Mechanics to High-Coordinate Actinide Complexes: Prediction of the Structures of Pu(IV), U(IV), Np(IV) and Th(IV) Hexanitrato Complexes" Moody, E. W.; Barr, M. E.; Jarvinen, G. D.; submitted to *Journal of Computational Chemistry*.

"QSAR of Distribution Coefficients for $Pu(NO_3)_6^{2-}$ Complexes using Molecular Mechanics" Moody EW, Barr ME, Jarvinen, GD; to be submitted to *Separation Science and Technology: Solvent Extraction and Ion Exchange*.

"Sorption of Pu(IV) from Nitric Acid by Bifunctional Anion-Exchange Resins" Bartsch, RA, Zhang ZY, Elshani S, Zhao W, Jarvinen GD, Barr ME, Marsh SF, Chamberlin RM; in preparation, to be submitted to *Separation Science and Technology: Solvent Extraction and Ion Exchange*.

"Plutonium (IV) Sorption by Soluble Anion-Exchange Polymers" Barr ME, Jarvinen GD, Moody EW, Vaughn RB, Bartsch RA; in preparation, to be submitted to *Separation Science and Technology: Solvent Extraction and Ion Exchange*.

"Trivalent Lanthinide and Actinide Sorption from Complex Mixtures using Anion Exchange" Barr ME, Jarvinen GD, Schulte LD, Stark PC, Chamberlin, RM; in preparation.

Presentations

“New Anion-Exchange Materials for Improved Separations of Nuclear Materials”, EMSP symposium, ACS- New Orleans, Aug. 1999.

"Americium Separations from Complex Mixtures using Anion Exchange" Barr ME, Jarvinen GD, Schulte LD, Stark PC, Chamberlin, RM; Abstracts of Papers of the American Chemical Society, v. 217 pp. 019-IEC MAR 21, 1999.

"Sorption of Pu(IV) from Nitric Acid by Bifunctional Anion-Exchange Resins" Bartsch, RA, Zhang ZY, Elshani S, Zhao W, Jarvinen GD, Barr ME, Marsh SF, Chamberlin RM; Abstracts of Papers of the American Chemical Society, v. 217 pp. 125-IEC MAR 21, 1999.

"QSAR of distribution coefficients for actinide hexanitrato complexes" Moody EW, Barr ME, Jarvinen GD; Abstracts of Papers of the American Chemical Society, v. 217(pt.2) pp. 170-NUCL MAR 21, 1999.

"Sorption of Pu(IV) by Soluble Anion-Exchange Polymers", Barr ME, Jarvinen GD, Moody EW, Vaughn RB; Abstracts of Papers of the American Chemical Society, v. 216(pt.2) pp. 88-NUCL AUG 23, 1998, and v. 216(pt.1) pp. 5-TECH AUG 23, 1998

"Development of Anion-Exchange Resins for Separations of Actinides", Barr ME, Jarvinen GD, Marsh SF, Bartsch RA; Abstracts of Papers of the American Chemical Society, v. 213(pt.2) pp. 73-IEC APR 13, 1997

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment", Marsh SF, Jarvinen GD, Bartsch RA, Nam J, Barr ME; Marc IV conference on Radioanalytical Chemistry, Kona, HI, April 1997