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PLUTONIUM(IV) SORPTION BY SOLUBLE ANION-EXCHANGE POLYMERS

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ABSTRACT

Soluble anion-exchange polymers have been designed, synthesized, and evaluated for their ability to take up Pu(IV) from nitric acid solutions. These polymers, based on linear poly(4-vinylpyridine) (PVP) and polyethyleneimine (PEI) are soluble in aqueous and strong acid solutions. Weak-base sites on the polymers are protonated under experimental conditions, and, in most cases, have been converted by alkylation to form mono- and bifunctional strong-base anion-exchange sites.

Distribution of Pu(IV) onto these polymers was determined by comparing visible spectroscopic data in the presence and absence of the soluble polymer. Overall plutonium affinity for the anion-exchange sites in the soluble materials is found to be much lower than for comparable solid resins, but the distribution behavior

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follows similar trends in that bifunctionalized materials are superior to monofunctionalized and a five-atom "spacer" between the two cationic sites is superior to other spacer lengths.

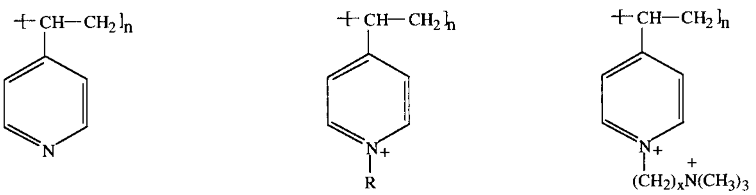
INTRODUCTION

Anion exchange in nitric acid is the preferred process for the recovery of plutonium from a variety of substrates. Spectroscopic studies of Pu(IV) in nitric acid sorbed onto ion-exchange media establish that the 12-coordinate hexanitrato complex is the species sorbed at the anion-exchange sites, regardless of the Pu(IV) speciation in solution (1–4). Of particular interest is the observation that Pu(IV) sorption onto the resin correlates best with the solution concentration of the uncharged tetranitrato complex (2), raising the possibility that Pu(IV) sorption occurs concurrently with the acquisition of two nitrato ligands. Individual monocationic sites of conventional anion-exchange resins are not configured optimally to either facilitate this process or bind the final dianionic complex. Thus, we have been developing bifunctional resins that we hope will facilitate the uptake process, providing superior binding properties and selectivity for dianionic complexes and exhibiting enhanced kinetics for plutonium uptake from solution.

Reillex HPQ®, a macroporous anion-exchange resin of partially methylated poly(4-vinylpyridine) (PVP) crosslinked with divinylbenzene (~25%), has been used at the Los Alamos National Laboratory Plutonium Facility for a number of years, since it exhibits superior resistance to both acid and radiolytic degradation. Our implementation of the bifunctionality concept evolved as N-derivatization of pyridinium units from similar base resins with a second cationic site such that the two anion-exchange sites are linked by "spacer" arms of varying length and flexibility.

Plutonium(IV) distribution coefficients (*D*s) for bifunctional resins synthesized from a low-crosslinked resin, Reillex 402® (2–4% divinylbenzene), have been reported (5,6), and a systematic study of the effects of crosslinking and derivatization upon more rigid resins is in progress. These materials have also proven effective in removing americium from high-salt nitric acid solutions (7,8). Herein, we compare plutonium affinity for analogous linear PVP systems, which are soluble polymers, to both the low-crosslinked (402) and higher-crosslinked (ca. 21% divinylbenzene, HP21) resins. Diagrams and nomenclature for the series of polymers are presented in Fig. 1.

We attempted to model the electrostatic interactions of the plutonium hexanitrato dianion with the bifunctional, dicationic site in order to determine if the precepts of "bite size", "preorganization", and "bidentate" can have an appreciable impact upon electrostatic bonding as they do for covalent bonding.



Base poly(4-vinylpyridine)
"PVP" = linear, soluble polymer
"402" = solid resin (2-4% divinylbenzene)
"HP21" = solid resin (21% divinylbenzene)

Quaternized, monofunctional
poly(4-vinylpyridine)
R = -H, $-CH_3$, $-CH_2CH_3$

Bifunctional poly(4-vinylpyridine)
x = 3 - 6 for PVP and HP21
x = 2 - 6 for 402

Figure 1. Structures for linear PVP polymers and solid resins (402 and HP21).

We had some success in correlating calculated electrostatic affinity in our model systems with experimental distribution coefficients (9), but were concerned at our need to assume that the dominant enthalpic and entropic terms for the transfer of plutonium from solution to the solid phase were relatively constant within a series of similar resins. Investigation of plutonium sorption by *soluble* anion-exchange polymers was motivated by our desire to decouple the effects of phase-transition enthalpy and kinetics from the weaker forces of electrostatic attraction. The energy for the transfer of plutonium from solution onto a soluble polymer was expected to be significantly smaller, allowing the electrostatic attraction to be a more dominant force. We observed this to be the case in that the distribution coefficients, *D*, for the soluble anion-exchange polymers are at least one order of magnitude lower than for comparable solid resins. However, within the limited scope of our investigation, we also found that the soluble systems exhibit *trends* in sorption behavior which are very similar to those observed in the solid resins.

EXPERIMENTAL

Soluble Polymer Synthesis

Polyvinylpyridine-based anion-exchangers were formed by reacting linear PVP, with commercially-available methyl iodide, ethyl bromide, or the appropriate *omega*-bromoalkyl-trimethylammonium bromide (10). The PVP was obtained directly from Reilly Industries (Indianapolis, IN) as Reillene®, a 25% solution in mixed alcohols (primarily methanol, ethanol, and 2-propanol) with a nominal molecular weight of 50,000.

Synthesis, purification, metathesis, and analysis of each polymer followed similar procedures. A sample procedure is described for synthesis of

PVP$-(CH_2)_3-N(CH_3)_3$. Solutions of $Br(CH_2)_3N(CH_3)_3$ (5.4 g, 0.024 mol) in denatured ethanol (5% 2-propanol) and Reillene (10.0 g containing approximately 2.5 g, 0.024 mol of PVP) were combined in a 250 mL two-neck round bottom flask outfitted with a heating mantle and a water condensor. The mixture was diluted to ca. 100 mL with additional ethanol and brought to a slow reflux. The reaction was allowed to continue over several days, approximately 60 hr. The solution was then reduced to dryness using a rotary evaporator, redissolved in water and lyophilized to form a fluffy pale pink solid. The level of substitution is estimated to be approximately 70% based on the peak area ratios for trimethylammonium to pyridinium and substituted pyridinium to unsubstituted pyridinium found in the ^1H NMR (D_2O). Elemental analysis of PVP$-(CH_2)_3-N(CH_3)_3Br_2$, calculated for 100% substitution: C, 42.65; H, 6.06; N, 7.65; FW = 366.14. Found: C, 43.68; H, 6.47; N 7.62; FW = 363.

Exchange of bromide with nitrate was achieved by dissolving ca. 0.25 g batches of polymer in 15 mL of an aqueous solution containing ~1.3 g of $NaNO_3$ (20+ equivalents). The solution was centrifuged in a Centriprep® (10,000 MW cutoff) tube at approximately 2500 cpm for 30 min. Two cycles with removal of eluate resulted usually in a five-fold volume reduction. The concentrated solution was diluted with deionized water and volume-reduced two times followed by a second treatment with $NaNO_3$/deionized (DI) water/DI water/DI water. The final solution was diluted with DI water and lyophilized to a fluffy, pale yellow solid. Elemental analysis of PVP$-(CH_2)_3-N(CH_3)_3(NO_3)_2$, calculated for 100% substitution: C, 47.27; H, 6.71; N, 16.96; FW = 330.34. Found: C, 48.07; H, 7.10; N, 15.12; FW (ave) = 348.

Proton NMR spectral data and CHN results for the PVP polymers are available as supplementary material. The permethylated polyethyleneimine (PEIM) used in this study was synthesized and analyzed using published procedures (11).

Spectroscopic Measurements

Plutonium distribution onto soluble polymers was determined from spectroscopic evaluation of Pu(IV) in nitric acid solutions in the presence and absence of the anion-exchange polymers. Optical absorption spectroscopy was performed with a Perkin–Elmer Lambda 9 spectrometer (PerkinElmer Analytical Instruments—USA, Shelton, CT) from 350 to 900 nm using a 0.5 nm step size and a 0.2 nm slit width.

Baseline visible spectra was measured for Pu(IV) in nitric acid solutions from 2.3 to 14.6 *M* at 0.5 molar intervals by titrating a solution of 2.3 *M* nitric acid with concentrated (15.6 *M*) nitric acid and a solution of concentrated nitric acid with 1.0 *M* nitric acid. Each solution contained initially 0.770 mL of Pu(IV)

(7.16 mg, 0.030 mmol) taken from a stock solution of 9.3 g/L Pu(IV) in 2.3 *M* nitric acid and added to 9.23 mL of the starting acid concentration. Solution concentrations of Pu(IV) varied from 3 to ca. 1.5 m*M* over the course of each titration. A MicroSoft Excel® spreadsheet was developed to determine the amount of titrant to be added in order to achieve the desired fixed spacings of 2.3, 3.0, 3.5, … , 13.5, 14.0, 14.6 *M* in nitric acid concentrations.

The visible spectrum of Pu(IV) remains virtually unchanged between 11.0 and 14.6 *M* nitric acid. This solution "endpoint" spectrum is the same as that observed for plutonium sorbed onto solid anion-exchange resins and has been ascribed to the hexanitrato complex (2).

Spectroscopic titration of plutonium solutions containing the nitrate form of the soluble polymers followed a similar procedure with the exception that the 9.23 mL of starting acid solution contained sufficient polymer such that the ratio of cationic sites (based on the number of nitrogen atoms) to Pu was ca. 100:1. For example, 0.532 g of $PVP-(CH_2)_3-N(CH_3)_3(NO_3)_2$ (1.5 mmol of polymer, 3.0 mmol of N) was dissolved in 2.3 *M* nitric acid to a volume of 9.23 mL. This large excess of polymer was used to achieve a solids to solution ratio similar to that used in the determination of the distribution of plutonium onto the solid resins (5,12), although the loading level of plutonium onto the soluble polymer is significantly lower. An additional advantage to using such a high polymer to plutonium ratio is that the effects of nonquantitative derivatization and uncertainties in the effective formula weight are minimized.

Spectra of the yellowish polymer solutions in nitric acid displayed smooth, featureless curves which were subtracted from each of the plutonium-containing spectra subsequent to their conversion to molar absorptivity-based spectra. In the case of the polyvinylpyridine derivatives, a single titration from 2.3 to ca. 7.5–8.5 *M* HNO_3 was sufficient to achieve the range from essentially no plutonium associated with the polymer to nearly quantitative sorption. In the case of the weaker-binding PEIM polymer, two titrations were required to cover the full range of acid concentrations for quantitative binding.

Plutonium Distribution Coefficient (*D*) Determination

Plutonium(IV) exists as a number of species over the range of nitric acid concentrations examined herein (2). While the visible spectral signatures of some plutonium species in nitric acid have been deconstructed from the complex spectra (13,14), it is not necessary to identify the individual species and their proportions to determine the distribution coefficients. The "baseline" spectra for plutonium in nitric acid provides the spectral signature associated with the equilibrium ratios of each complex at specific acid concentrations. Thus, any "free" plutonium that is not sorbed by the anion-exchange polymer should exhibit the same signature spectrum. Plutonium(IV) “bound” to the anion-exchange sites of the soluble polymers is expected to exhibit complexation behavior similar to that observed for analogous solid resins, i.e., it would be associated as the $Pu(NO_3)_6^{2-}$ anion only. Since the absorbance spectra for the plutonium hexanitrato complex is not significantly perturbed by association with the resin sites, the solution spectrum of Pu(IV) in 14.0 *M* nitric acid was selected as the basis spectrum for plutonium bound to the anion-exchange sites of the polymer. Thus, the spectrum of plutonium(IV) in the presence of polymer becomes a simple two-component system in which the contributions to the spectrum from the “free” and “bound” plutonium total 100%.

Although the spectral features of the plutonium hexanitro complex sorbed to anion-exchange sites of the polymer would not be necessarily *identical* to the features of the complex in nitric acid, we find that this simple two-component approach works quite well. For example, Fig. 2b shows the spectrum of Pu(IV) and $PVP-(CH_2)_4-N(CH_3)_3(NO_3)_2$ in 5.0 *M* nitric acid. One can see readily that it comprises approximately equal contributions from free Pu(IV) as shown in spectrum 2c and bound Pu(IV) as represented by spectrum 2a of Fig. 2.

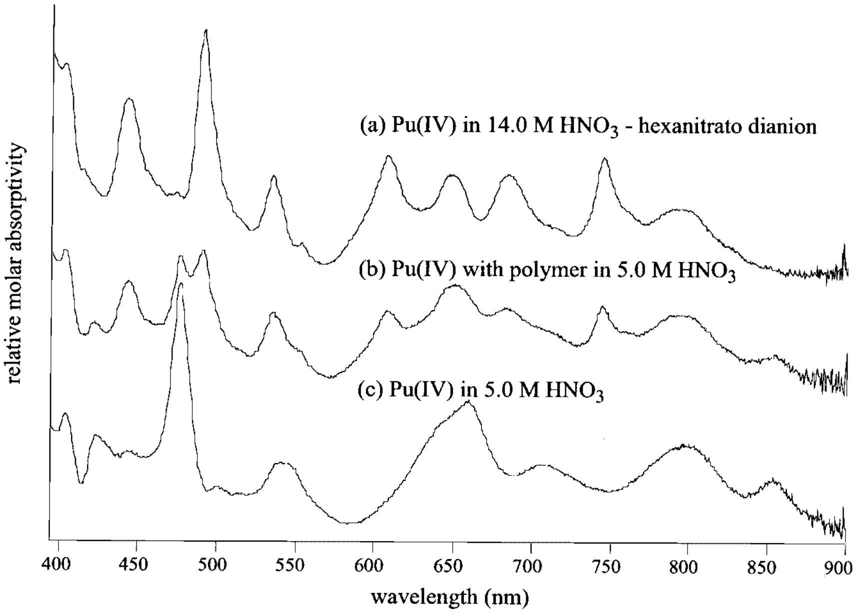


Figure 2. Representative spectra for Pu(IV) in nitric acid in the presence (b) and absence (c) of soluble polymer $PVP-(CH_2)_4-N(CH_3)_3$. The spectrum of Pu(IV) in 14.0 *M* nitric acid (a) is used as the basis spectrum for plutonium bound to the polymer anion-exchange sites.

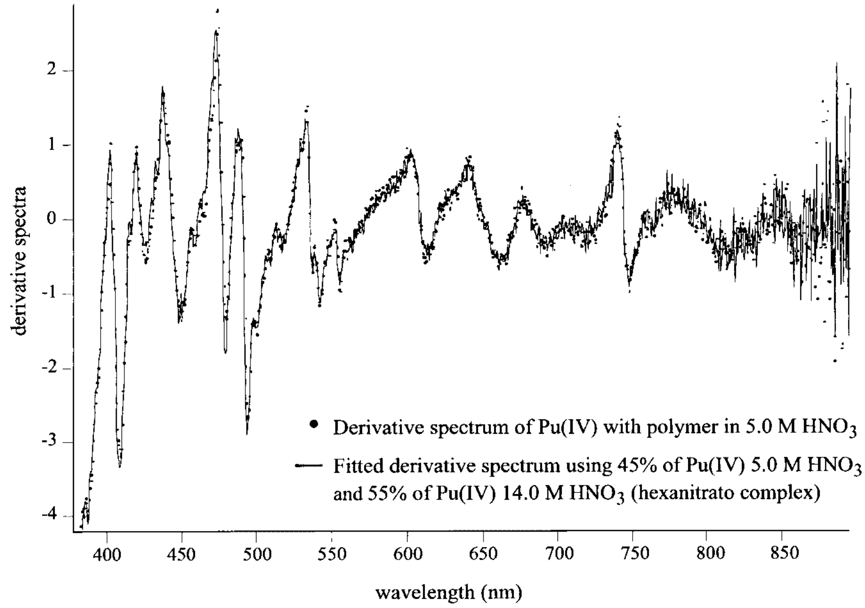


Figure 3. First derivative spectra (raw and fitted) for Pu(IV) with PVP–$(CH_2)_4$–$N(CH_3)_3$ in 5.0 *M* nitric acid.

Since there is some baseline drift, particularly at shorter wavelengths, it is more precise to fit the data as first derivative spectra. As seen in Fig. 3, the fits to the derivative spectra were quite good and only minimal smoothing of the spectral components was necessary to reduce scatter. Manual data fitting was performed by adjusting the spectral contribution (fraction) of free and bound plutonium. Manual fitting of the spectral data was far more satisfactory than automated fitting programs since, in some cases, there were small shifts in the wavelength of peak maxima. Manual fitting also allowed more attention to be paid to the *shapes* of the curves and to focus on areas of the greatest spectral diversity. In general, changes in the two-component composition by greater than 2% resulted in a noticeably poorer fit.

Although the use of mL/g is unusual for calculations in single-phase systems, we use these units to assist in correlating the behavior of the soluble anion-exchangers with their insoluble analogues. Distribution coefficients for plutonium onto the soluble anion-exchange polymers were calculated as shown below:

$$D = \frac{[\mathrm{Pu}]_{\mathrm{b}} S}{[\mathrm{Pu}]_{\mathrm{f}} A}$$

where $[Pu]_b$ is the fraction of bound Pu, $[Pu]_f$ the fraction of free Pu, S the milliliters of solution contacted, and A the grams (dry) of polymer used.

Uncertainties in the calculated D values are derived primarily from the qualitative aspect of the spectral fits. They range from less than 8% for *D*s near 20 (approximately 50% bound) to over 100% for regions where there is near-quantitative binding ($>95\%$ bound, $D > 500$). Therefore, these values are most appropriately used in qualitative fashion. For this series of experiments, the internal consistency of the methods used for the seven soluble polymers and the determination of sorption behavior over a broad range of acid concentrations should minimize the effects of experimental uncertainties upon comparison of their *relative* performances.

Ideally, our distribution measurements onto soluble polymers could be confirmed by use of ultrafiltration to separate bound from unbound plutonium physically. However, in this case, the extremely oxidizing high-acid media precludes a physical separation, and we must rely upon a less rigorous analysis of the combined system.

RESULTS AND DISCUSSION

The summary of the D values for plutonium onto the soluble anion-exchange polymers as a function of nitric acid concentration is presented in Table 1. In general, there is very little difference in performance between the three mono-functionalized PVP polymers: the protonated, methylated, and ethylated polyvinylpyridines. However, as displayed in Fig. 4, the four bifunctional soluble polymers display an enhanced plutonium affinity as well as systematic differences in their individual behaviors. The affinity of the plutonium hexanitrato complex for the polymer increase initially as the spacer is lengthened, reaches its maximum value with the 1,5-pentylene spacer, then decreases. This trend is virtually identical to that observed for the analogous HP21 series of resins (12), and is only slightly different from the behavior observed for the 402 series where the bifunctional resin with the 1,5-pentylene spacer also outperforms the corresponding butylene resin, but to a lesser extent (5). Figure 5 summarizes the D values for the soluble and solid resins in 7.0 M nitric acid. Note that the D values for plutonium onto the two solid resins are similar in magnitude (left axis) despite the significant difference in the crosslinking of the substrate (2–4% divinylbenzene for the 402 resin vs. 21% for the HP21 resin). The D values for the soluble bifunctional polymers are approximately one order of magnitude lower (right axis).

The PVP-based polymers exhibit significantly higher plutonium affinity than the PEIM polymer consistently. Although PEIM is a branched, agglomerated polymer, its high charge density (one in every three nonhydrogen

Table 1. Experimentally-Determined Distribution Coefficients for Pu(IV) with Soluble Polymers as a Function of Nitric Acid Concentration. Percent of Pu(IV) Bound Is Given in Parentheses

HNO_3(M)	PVP	PVP–CH_3	PVP–CH_2CH_3	PVP–$(CH_2)_3$–$N(CH_3)_3$	PVP–$(CH_2)_4$–$N(CH_3)_3$	PVP–$(CH_2)_5$–$N(CH_3)_3$	PVP–$(CH_2)_6$–$N(CH_3)_3$	PEIM
2.3			0.69 (4)	0.38 (2)	0.99 (5)	0.94 (5)	(0)	
3.0	1.1 (5)		0.93 (5)	1.5 (7)	1.5 (7)	2.8 (13)	1.7 (8)	
3.5	2.9 (12)	1.6 (10)	1.8 (9)	3.6 (15)	3.6 (15)	6.2 (24)	3.5 (15)	
4.0	7.4 (25)	3.8 (20)	4.2 (18)	7.6 (26)	7.2 (25)	12.1 (37)	7.7 (27)	2.0 (8)
4.5	13.6 (37)	7.2 (31)	9.4 (32)	17.7 (44)	15.0 (40)	24.2 (53)	16.4 (43)	3.2 (12)
5.0	24.3 (50)	13.7 (45)	18.5 (47)	28.8 (55)	27.7 (54)	36.7 (62)	34.0 (60)	4.7 (16)
5.5	41.6 (62)	26.4 (60)	35.8 (62)	60.6 (71)	52.6 (68)	83.7 (78)	58.2 (71)	7.8 (23)
6.0	65.8 (71)	55.6 (75)	69.3 (75)	78.2 (75)	98.0 (79)	153 (86)	99.9 (80)	13.5 (33)
6.5	107 (79)	89.0 (82)	97.5 (80)	117 (81)	201 (88)	236 (90)	149 (85)	19.3 (40)
7.0	146 (83)	138 (87)	146 (85)	194 (87)	261 (90)	527 (95)	250 (90)	28.3 (48)
7.5	257 (89)	291 (93)	246 (90)	277 (90)	586 (95)	952 (97)	560 (95)	39.8 (55)
8.0	390 (92)	1147 (98)	554 (95)	625 (95)				52.0 (60)
8.5	690 (95)							86.7 (70)
9.0								120 (75)
9.5								245 (85)
10								896 (95)

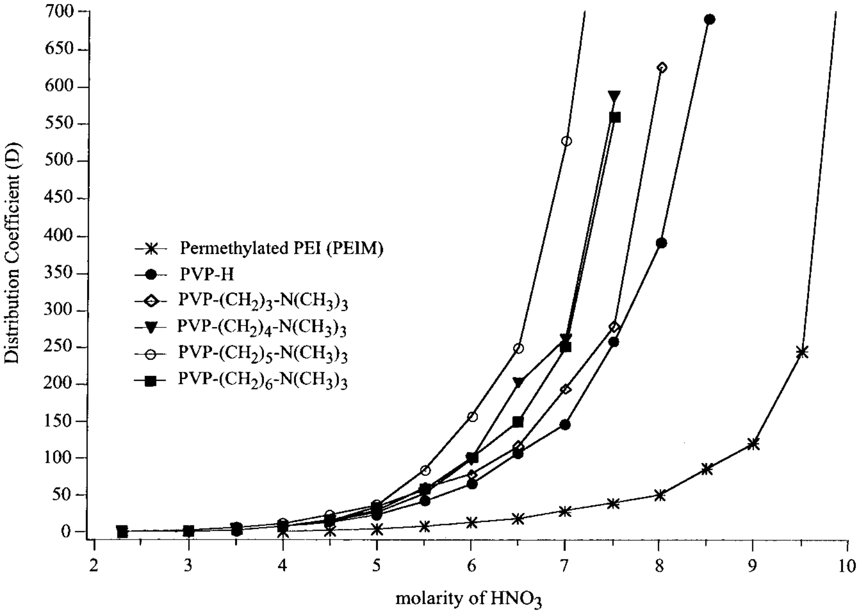


Figure 4. Pu(IV) distribution coefficient vs. nitric acid concentration for selected monofunctional and bifunctional PVP polymers and permethylated PEIM in 7.0 *M* HNO_3.

atoms is a quaternary amine) makes the system far less lipophilic than the linear polyvinylpyridines. Thus it is possible that the lower *D*s for Pu on PEIM reflect a decreased enthalpic favorability for sorption of the relatively lipophilic hexanitrato complex.

Linear PVP and its quaternized salts exhibit varied and intriguing solution properties. Despite being completely miscible with water, the resulting systems cannot be considered truly monophasic. Under relatively dilute conditions ($I = 0.001-1\,M$), the radii of gyration, R_g, of the polymers decrease with increase in ionic strength, indicating coiling and intramolecular interactions which expel water (15). This behavior is most notable for polymers with lipophilic alkyl groups. Similar conformational changes occur when monovalent anions are displaced by divalent anions (16). Certain alkylated derivatives act as polysoaps and form micellar agglomerates or precipitate from aqueous solutions near their isoelectric point (17,18), so intermolecular interactions can lead to nonhomogenous dispersal in solutions certainly.

We do not, as yet, have information on the conformational changes or agglomerations that may occur with these anion-exchange polymers in strong nitric acid. However, the solution absorbance spectra did not exhibit changes in

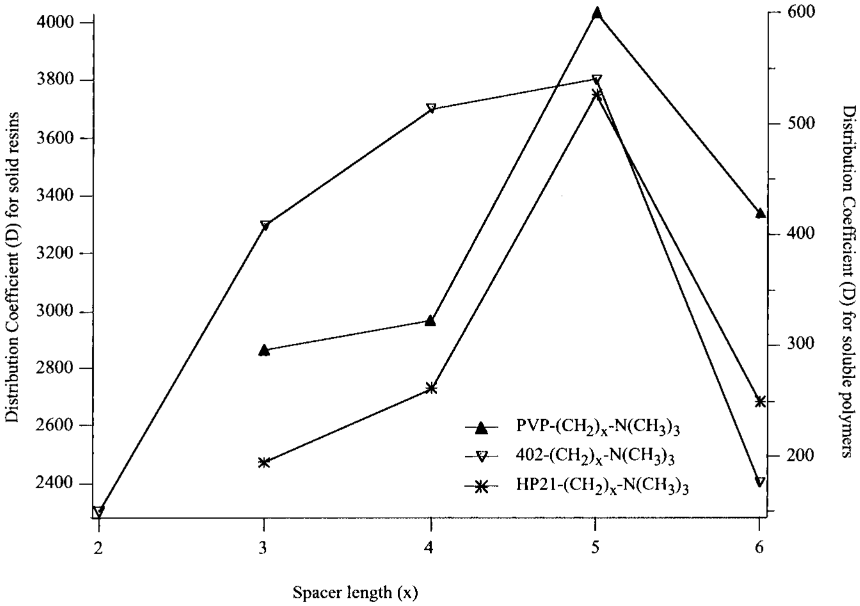


Figure 5. Pu(IV) distribution coefficients for solid (left axis, 6 hr) and soluble (right axis, equilibrium) polymers. Full data for the 402–$(CH_2)_x$–$N(CH_3)_3$ and HP21–$(CH_2)_x$–$N(CH_3)_3$ series are provided in Refs. (5,12), respectively.

absorbance at shorter wavelengths indicative of the formation of a separate phase sufficiently large to scatter the incident energy. Thus, it appears that the polymers exhibit a relatively constant physical state over the range of nitric acid solutions examined here.

While the sorption of Pu(IV) onto soluble anion-exchange polymers is unlikely to be a *completely* monophasic process, the Gibbs energy of phase transfer, ΔG_{tr}, is probably very close to a constant for the series of bifunctional resins PVP–$(CH_2)_x$–$N(CH_3)_3$, $x = 3–6$. In general, anion radius and charge are the fundamental ion properties that affect ion-exchange selectivity (19). Assuming that the mechanism of plutonium sorption into the polymers is the same for all members of the series, these properties are constant. Thus, we believe the primary difference in binding of the plutonium hexanitrato dianion to the various polymers is due to weak anion-recognition based on the conformation of the bifunctional site. In studies of bifunctional cation/anion interactions in systems selected for strain-free contact, it was concluded similarly that entropic disadvantages of longer spacer lengths could be offset by enthalpic advantages, such as a slightly better fit with more flexible systems (20).

CONCLUSIONS

In previous studies, we established a correlation between plutonium distribution and calculated dianion/dication electrostatic forces for the 402-series of bifunctional solid resins (9). However, the correlation between the calculated electrostatic forces (stickiness factor) and Gibbs free energy associated with the process was not well defined. Here, we have virtually eliminated a major component, the Gibbs energy of phase transfer, and observe that the soluble systems exhibit *trends* in sorption behavior which are very similar to those for analogous solid resins. We attribute the observed differences in sorption response to weak anion-recognition between the plutonium hexanitrato dianion and the bifunctional cationic site. The one order of magnitude difference in the D values between the soluble anion-exchange polymers and comparable solid resins most likely reflects the difference in phase-transfer energies associated with monophasic vs. biphasic transfer.

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REFERENCES

1. Ryan, J.L. Species Involved in the Anion Exchange Absorption of Quadrivalent Actinide Nitrates. J. Phys. Chem. **1960**, *64*, 1375–1385.
2. Marsh, S.F.; Day, R.S.; Veirs, D.K. *Spectrophotometric Investigation of the Pu(IV) Nitrate Complex Sorbed by Ion-Exchange Resins*. LA-12070; Los Alamos National Laboratory: Los Alamos, NM, 1991.
3. Viers, D.K.; Smith, C.A.; Berg, J.M.; Zwick, B.D.; Marsh, S.F. Characterization of the Nitrate Complexes of Pu(IV) Using Absorption Spectroscopy, ^{15}N NMR, and EXAFS. J. Alloys Compd **1994**, *213/214*, 328–332.
4. Allen, P.G.; Veirs, D.K.; Conrandson, S.D.; Smith, C.A.; Marsh, S.F. Characterization of Aqueous Plutonium(IV) Nitrate Complexes by

Extended X-Ray Absorption Fine Structure Spectroscopy. Inorg. Chem. **1996**, *35*, 2841–2845.

5. Marsh, S.F.; Jarvinen, G.D.; Bartsch, R.A. New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment. React. Funct. Polym. **1997**, *35*, 75–80.
6. Marsh, S.F.; Jarvinen, G.D.; Bartsch, R.A.; Nam, J.; Barr, M.E. New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment, Part II. J. Radioanal. Nucl. Chem. **1998**, *235* (1–2), 37–40.
7. Barr, M.E.; Schulte, L.D.; Jarvinen, G.D.; Espinoza, J.; Ricketts, T.E.; Valdez, Y.; Abney, K.D.; Bartsch, R.A. Americium Separations from Nitric Acid Process Effluent Streams. J. Radioanal. Nucl. Chem. **2001**, *248* (2), 457–465.
8. Barr, M.E.; Jarvinen, G.D.; Stark, P.C.; Chamberlin, R.M.; Bartsch, R.A.; Zhang, Z.-Y.; Zhao, W. Americium Separations from High-Salt Solutions Using Anion Exchange. Sep. Sci. Technol. **2002**, *36* (12), 2609–2622.
9. Moody, E.W.; Barr, M.E.; Jarvinen, G.D. QSAR of Distribution Coefficients for $Pu(NO_3)_6^{2-}$ Complexes Using Molecular Mechanics. J. Radioanal. Nucl. Chem. **2001**, *248* (2), 431–437.
10. Bartsch, R.A.; Zhao, W.; Zhang, Z.Y. Facile Synthesis of (Omega-Bromoalkyl) Trimethylammonium Bromides. Synth. Commun. **1999**, *29* (14), 2393–2398.
11. Shkinev, V.M.; Spivakov, B.Y.; Geckeler, K.E.; Bayer, E. Anion-Exchange Extraction and Enrichment from Aqueous-Solutions by Quaternary Ammonium Reagents. Solvent Extr. Ion Exch. **1989**, *7* (3), 499–510.
12. Bartsch, R.A.; Zhang, Z.Y.; Elshani, S.; Zhao, W.Y.; Jarvinen, G.D.; Barr, M.E.; Marsh, S.F.; Chamberlin, R.M. Sorption of Pu(IV) from Nitric Acid by Bifunctional Anion-Exchange Resins. In *Abstracts of Papers, Part 1,* 217th National Meeting of the American Chemical Society, Anaheim, CA, March 21–25; American Chemical Society: Washington, DC, 1999; IEC-125.
13. Berg, J.M.; Veirs, D.K.; Vaughn, R.B.; Cisneros, M.R.; Smith, C.A. Plutonium(IV) Mononitrate and Dinitrate Complex Formation in Acid Solutions as a Function of Ionic Strength. J. Radioanal. Nucl. Chem. **1998**, *235* (1–2), 25–29.
14. Berg, J.M.; Veirs, D.K.; Vaughn, R.B.; Cisneros, M.R.; Smith, C.A. Speciation Model Selection by Monte Carlo Analysis of Optical Absorption Spectra: Plutonium (IV) Nitrate Complexes. Appl. Spectrosc. **2000**, *54* (6), 812–823.
15. Beer, M.; Schmidt, M.; Muthukumar, M. The Electrostatic Expansion of Linear Polyelectrolytes: Effects of Gegenions, Co-ions, and Hydrophobicity. Macromolecules **1997**, *30*, 8375–8385.

16. Tricot, M.; Houssier, C.; Desreux, V. Electro-optical Studies of Synthetic Polyelectrolytes: Part II—Electric Birefringence of Poly-*n*-butyl-4-vinylpyridinium Salts in Aqueous Solutions. Eur. Polym. J. **1976**, *12*, 575–583.
17. Strauss, U.P.; Gershfeld, N.L.; Spiera, H. Charge Reversal of Cationic Poly-4-vinylpyrdine Derivatives in KBr Solutions. J. Am. Chem. Soc. **1954**, *76*, 5909–5911.
18. Strauss, U.P.; Gershfeld, N.L. J. Phys. Chem. **1954**, *58*, 747–753.
19. Moyer, B.A.; Bonnesen, P.V. *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Garcia-Espana, E., Eds.; Wiley–VCH: New York, 1997; 1–44.
20. Houssain, M.A.; Schneider, H.-J. Physical Factors in Anion Separations. In Supramolecular Chemistry, Part 85[+]: Flexibility, Association Constants, and Salt Effects on Organic Ion Pairs: How Single Bonds Affect Molecular Recognition. Chem. Eur. J. **1999**, *5* (4), 1284–1290.

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