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New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment-

Part II

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Abstract

Additional bifunctional anion-exchange resins have been designed, synthesized and evaluated for their ability to take up Pu(IV) from nitric acid solutions. Bifunctionality is achieved by adding a second anion-exchange site to the pyridine nitrogen (also an anion-exchange site) of the base poly(4-vinylpyridine) resin. Previous work focused on the effect of varying the chemical properties of the added site along with the length of an alkylene 'spacer' between the two sites. Here we examine four new 3- and 4-picolyl derivatives which maintain more rigidly defined geometries between the two nitrogen cationic sites. These materials, which have the two anion-exchange sites separated by three and four carbons, respectively, exhibit lower overall Pu(IV) distribution coefficients than the corresponding N-alkylenepyridium derviatives with more flexible spacers. Methylation of the second pyridium site results in a ca. 20% increase in the Pu(IV) distribution coefficients.

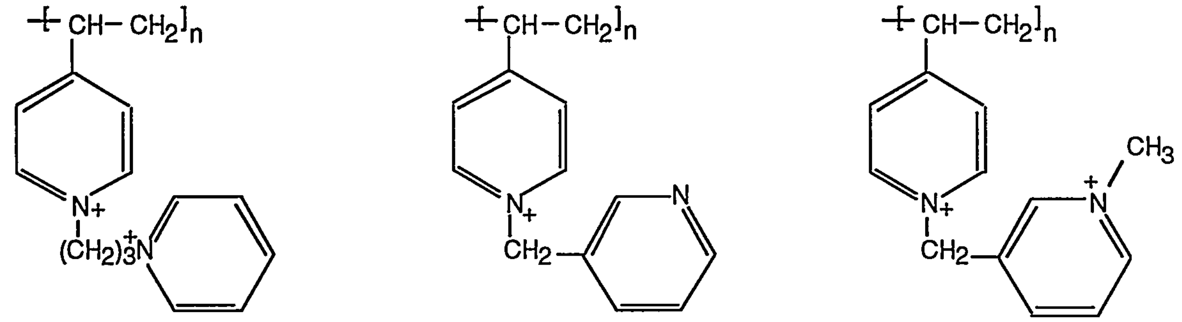
Introduction

Spectroscopic studies of plutonium (IV) in nitric acid solution and sorbed to ion-exchange media revealed that while the dianionic hexanitrato complex is the species sorbed onto anion exchange resins,[1] Pu(IV) sorption onto the resin correlates best with the solution concentration of the *uncharged* tetranitrato complex.[2,3] Therefore, it is the most likely species to be sorbed onto the resin, acquiring two nitrate groups in the process. Commercially available anion-exchange resins have a single cationic charge at each active site. For multiply charged anions, interaction with two or more sites usually occurs with displacement of more weakly held anions. In the case of the plutonium nitrato complexes, however, the two 'displaced' nitrates may become incorporated into the inner coordination sphere of the plutonium (IV). Isolated monocationic sites are not optimally configured to facilitate this process nor to bind the final dianionic hexanitrato Pu(IV) complex. We hypothesized that a resin which could facilitate the uptake process, for example, by positioning the two nitrate groups in the proper configuration, would provide superior binding properties and selectivity for plutonium nitrato complexes and exhibit enhanced kinetics for plutonium uptake from solution.

Our implementation of the bifunctionality concept involves N-derivatization of pyridinium units from a base poly(4-vinylpyridine) resin with a second cationic site such that the two anion-exchange sites are linked by 'spacer' arms of varying length and flexibility. It is, to some extent, an attempt to extend the principles developed for ion-specific chelating ligands to the outer coordination-sphere of the plutonium nitrato complexes. These materials, and their underlying methodologies, differ significantly from bifunctional resins of Alexandratos, *et. al.*,[4] where two functionalities are appended as discrete pendent groups to a base polystyrene resin and are selected for their abilities to interact in a complementary, or synergistic, fashion.

To begin testing our 'facilitated uptake' hypothesis, and in the hope of developing improved anion-exchange material for nuclear waste treatment, we synthesized and tested several series of bifunctional anion-exchange materials which were derivatives of Reillex® 402 poly(4-vinylpyridine) resin. The results of these experiments have been previously reported.[5] It was found that the bifunctional resins exhibited plutonium distribution coefficients (Kd's) which are 5-10X than those obtained for the monocationic Reillex® HPQ. The optimal alkylene 'spacer' length appears to be five atoms, with etherate linkages outperforming alkyl linkages. The order of affinity for Pu(IV) from 7 M nitric acid was N-pyridinium > P-phosphonium > N-ammonium for the series tested. A recent, complementary, study has shown that akyl and etherate 'spacer arms' between the quaternary ammonium functionality and the benzene ring of more conventional anion-exchange resins generally improves thermal, radiolytic and chemical stabilities.[6] Enhanced resin stability under high-acid, high radiation conditions has been a major consideration in our selection of polyvinylpyridine as the 'base' resin and the specific functionalities appended.

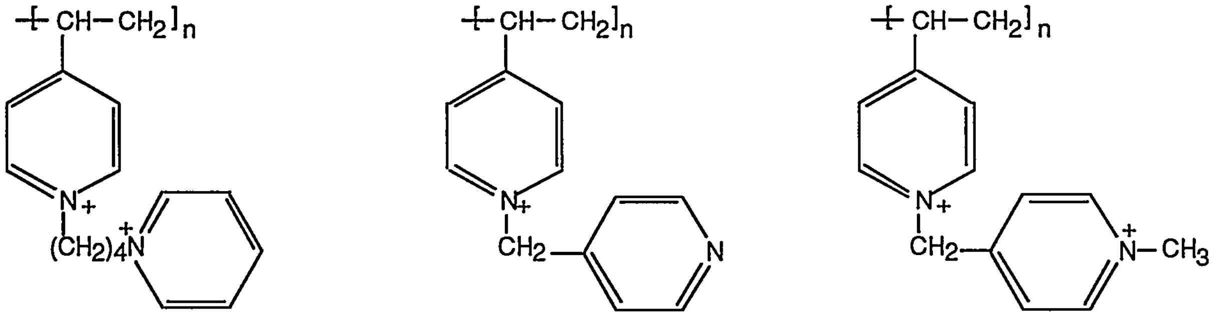
Given the unusually high Kd's exhibited by the N-alkylenepyridinium derivatives and their anticipated high level of chemical and radiolytic stability, we synthesized and evaluated an second set of bifunctional resins based on picolyl-substituted 4-vinylpyridine polymers. Besides the different pyridium linkage chemistry (C- vs. N-), these new materials maintain more rigidly constrained distances and orientations between the two nitrogen cationic centers than the previous materials. Structures of the active exchange sites are shown below (Fig.1).



Poly(N-propylenepyridinium 4-vinylpyridinium)

3-picolyl substituted poly(4-vinylpyridinium)

methylated 3-picolyl substituted poly(4-vinylpyridinium)



Poly(N-butylenepyridinium 4-vinylpyridinium)

4-picolyl substituted poly(4-vinylpyridinium)

methylated 4-picolyl substituted poly(4-vinylpyridinium)

Fig. 1. Experimental bifunctional resins.

Experimental

Samples of Reillex® 402 resin (Reilly Industries) were reacted with 3- and 4-picolylchloride by refluxing in methanol at elevated pressure. Portions of the resulting resins were then reacted with a small excess of methyl iodide to produce the corresponding N-methylated materials.

Plutonium distribution coefficients were measured and calculated by streamlined procedures developed at Los Alamos National Laboratory.[7] Initial contact solutions contained 3 g/L plutonium in 1-9 M nitric acid. We measured Kd values for dynamic contact periods of 30 min, 2 hr, and 6 hr to obtain information about the sorption kinetics. The 129-keV gamma-ray peak of ^{239}Pu was measured in all solutions, both before and after contact with the resin. The difference between these two measurements represented the quantity of plutonium sorbed on the resin. The Kd values for each contact was calculated as follows:

$$Kd = \frac{Pr-Po}{Po}\,\frac{S}{A}$$

where Pr = measured precontact activity
Po = measured postcontact activity
S = milliliters of solution contacted
A = grams (dry) of resin contacted

We estimate the uncertainties associated with the reported Kd values to range from 10-20%.

Results and Discussion

The measured Kd values for the 3- and 4-picolyl substituted resins and their N-methylated derivatives are presented in Table 1. The performance of our new materials was previously compared[7] to the monocationic Reillex® HPQ resin (N-methyl-4-vinylpyridine, 25% crosslinked with divinylbenzene). We have recently determined Kd values for the lower crosslinked Reillex® 402 resin (2-4% divinylbenzene) used as the base resin for our bifunctional derivatives. Comparative data for the base resin and for the n=3 and n=4 N-alkylenepyridium derivatives measured previously[5] are also provided in Table 1.

In 7 M nitric acid, all of the bifunctional resins surpass the Kd values for Pu(IV) obtained for the base resin. Under acidic conditions, unfunctionalized pyridine sites are protonated and can act as weak-base exchange sites. Methylation of the added pyridine nitrogen, as in going from the

3-picolyl to the N-methyl-3-picolyl derviative and the 4-picolyl to the N-methyl-4-picolyl derviative, converts these weak-base sites to strong-base sites with a corresponding ca. 20% improvement in plutonium sorption from high-acid solutions. This improved performance is somewhat greater than that observed for methylation of the base resin. Studies are currently underway to address this issue.

Comparison of the two 3-picolyl substituted resins with the N-propylenepyridium substituted resin shows that, for the same number of 'spacer' carbons, the more rigid species display decreased plutonium affinity in 7-9 M nitric acid. The effect is even more pronounced for the four carbon linkages. The presumption is that the orientation of the two cationic sites of the rigid spacers is sub-optimal and flexible linkages allow a more energy-minimized configuration. We are currently testing this hypothesis by molecular modeling of the complex cation-anion interactions as well as by synthesis and testing of other 'rigid' systems.

The kinetics of plutonium sorption from nitric acid for the bifunctional resins are somewhat slower than for the base resin in that the Kd values for the bifunction resins continue to increase between 2 and 6 hours. Of the initial resins tested,[5] only the trimethyl ammomium derivatives displays faster kinetics for plutonium uptake does than the base resin. Those materials generally reached their maximum values within the first 30 minutes of contact. Among the remaining bifunction resins, however, we observe few systematic differences which can be attributed to specific functionalities.

Conclusions

These new bifunctional anion-exchange resins are extremely effective at removing Pu(IV) from nitric acid solution. The high '30 minute' distribution coefficients are particularly advantageous for high-throughput operations, such a waste-stream polishing, where the actual metal-resin contact time is very short. As with most heterogenous systems, fully isolating all the factors involved in plutonium sorption onto anion-exchange resins will require combining empirical experimental data with theoretical modeling calculations.

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Table. 1. Distribution coefficients (Kd's) for Pu(IV) from nitric acid.

[HNO_3] (Molar)	Contact time (hr)	Reillex® 402[a]	Propylene pyridinium[b]	Butylene pyridinium[b]	3-picolyl	4-picolyl	Methylated 3-picolyl	Methylated 4-picolyl
1	0.5	1.0	0.9	1.5	1.9	1.2	1.2	-
	2	1.9	1.5	1.7	1.5	1.3	1.2	-
	6	2.2	1.1	1.5	1.6	1.2	1.7	-
3	0.5	-	52	-	61	51	-	-
	2	-	54	92	72	60	62	-
	6	-	56	100	74	60	64	45
5	0.5	-	790	-	660	580	720	640
	2	-	790	1000	950	750	820	780
	6	-	820	1400	1000	890	859	790
7	0.5	1258	5100	-	3100	3800	3800	4000
	2	2635	4700	4700	4300	4400	5900	5400
	6	2591	5600	11,000	5300	4800	6900	6400
9	0.5	-	5900	-	4300	4900	7800	8000
	2	-	9400	6200	7700	5600	7700	8500
	6	-	9600	7700	8700	7500	9100	12,000

[a] Values for the base resin, Reillex® 402, are presented for comparison. [b] Values for the propylene- and butylenepyridinium substituted poly(4-vinylpyridium) resins are from ref. 5.