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Fundamental Studies of Polymer Filtration

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Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The objectives of this project were (1) to develop an enhanced fundamental understanding of the coordination chemistry of hazardous-metal-ion complexation with water-soluble metal-binding polymers and (2) to exploit this knowledge to develop improved separations for analytical methods, metals processing, and waste treatment. We investigated features of water-soluble metal-binding polymers that affect their binding constants and selectivity for selected transition metal ions. We evaluated backbone polymers using light scattering and ultrafiltration techniques to determine the effect of pH and ionic strength on the molecular volume of the polymers. The backbone polymers were incrementally functionalized with a metal-binding ligand. A procedure and analytical method to determine the absolute level of functionalization was developed and the results correlated with the elemental analysis, viscosity, and molecular size.

Background

The need for new advanced metal separations technologies is evident not only within the Department of Energy (DOE) complex but also within other governmental agencies such as the Department of Defense (DoD) and the Environmental Protection Agency (EPA), as well as within private industries. This need may be driven by a variety of reasons ranging from environmental remediation, regulatory restrictions, economics, resource conservation and/or waste minimization. Over the past twelve years Los Alamos National Laboratory (LANL) has had an active inter-divisional program involved in ligand-design and synthesis for metal separations and the development of new separations technologies. Solvent extraction, chelating resins, ion-exchange, electrodialysis and Polymer Filtration™ are among some of the technologies being developed, evaluated, and commercialized for a wide range of metal recovery applications.

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Polymer Filtration™ (PF) has emerged as one of the more promising technologies for dilute metal-ion separations.¹ PF involves the use of water-soluble metal-binding polymers in combination with ultrafiltration as a means for the separation, concentration, and recovery of metals ions in dilute aqueous solutions. By selectively binding the target metals with soluble, large molecular weight polymers, the effective size of the metals can be temporally increased, and separations can be accomplished by size-exclusion ultrafiltration. Much smaller unbound species in solution, which includes solvent, innocuous metals (i.e., Na, K, etc.) and other solutes readily pass through the membrane. The polymer-metal complex, too large to pass through the pores of the filter, are retained. After ultrafiltration, the metals can be released from the polymer by several methods, the most common being pH adjustment. They are free to pass through the membrane to be collected in a concentrated form. The polymer may then be recycled for additional metal ion recovery.

The advantages of PF over other technologies is that metal binding takes place in a homogeneous solution which provides for very rapid kinetics. No requirements are placed on the mechanical stability of the polymers (unlike ion-exchange) and since metal binding takes place in aqueous solution, there is no need for organic solvents (unlike liquid-liquid extraction). As in liquid-liquid extraction, Polymer Filtration™ is a single contact between the polymer and the metal ion-containing solution and therefore the efficiency of binding must be high for effective metal selectivity and retention. For this reason the key to efficient, selective separation of metals using polymer filtration is in the *stability of the polymer-metal complex*.

Stability constants are equilibrium constants for metal-ion complexation and is a measure of the affinity a ligand (L) has for metal ions (M) in solution. The greater the stability of the ligand-metal complex, the further to the right the equilibrium is shifted favoring the formation of a complex:

One such way to increase the stability constant of a metal complex is to introduce *preorganization* into the binding system. Preorganization physically ties more than one ligand together in such a way that the ligands can easily participate in a cooperative effort in the binding of a metal ion. Such an effect, often called the chelate effect, usually results in a marked increase in the stability of the metal complex. The advantages in

preorganization are most evident in biological systems where naturally occurring ionophores and siderophores show very high binding constants with a great deal of selectivity.²

The use of water-soluble metal-binding polymers with ultrafiltration is a relatively new approach for metal-ions separations and up to now has never been used in the commercial sector³. We have extended the use of water-soluble chelating polymers to a variety of applications using a broad range of chelators and backbone polymers.

Scientific and Technical Impact

Polymer Filtration™ has the potential for very broad applications in the area of metal-ion recovery. Success in this area has already been demonstrated in electroplating applications. This application improves industrial competitiveness for the electroplating industry by minimizing metal losses to waste sludges from the electroplating processes. In addition, industrial liability is reduced, energy saved, and ultimately, an economic saving is realized.

The development of new polymers for the selective recovery of metal ions are needed for application of PF technology to more challenging metal-ion waste stream problems (solution mining, photographic effluent, nuclear power plant waste water, cooling waters). Proper polymer formulations will ready this technology for commercialization in these and other areas. Along with the new polymers is the need to understand the coordination chemistry, level of functionalization, and other quality control factors.

Aminodicarboxylate chelating ion exchange resins are available commercially (e.g., Chelex 100, BioRad) having been first prepared by Hale et.al. and Pepper et. al. and shown to be very selective.⁴ Geckeler⁵ has reported the preparation and use of aminodicarboxylate-containing water-soluble polymers for metal binding and separation. From literature reports the level of functionalization with the dicarboxylate is not clear, nor has the impact of systematically varying the level of functionalization on the polyamine on the physical and metal-binding properties of the polymer been reported. We report here on the preparation and characterization of a series of water-soluble chelating polymers based on the aminodicarboxylate functionality.

Experimental

Polyamine was reacted with varying equivalents of chloroacetic acid or sodium chloroacetate (Fluka) to produce the carboxylated polymers. The reactions were performed in water (400 mL) in a three-neck round-bottom reaction flask equipped with a heating mantle, mechanical stirrer, thermometer and pressure-equalizing addition funnel exchanged for a condenser later in the reaction. The polymer, chloroacetic acid (or sodium chloroacetate), and sodium hydroxide (J.T. Baker) (if used) were weighed into Erlenmeyer flasks and dissolved in deionized water. The polymer and chloroacetic acid (or chloroacetate) solutions were added to the round-bottom flask, the sodium hydroxide was added dropwise over a 30-minute period to the stirring polymer/chloroacetate solution, keeping the temperature below 50°C during the addition. After the addition was finished the addition funnel was replaced with a condenser and the reaction solution was refluxed for three hours (94-96°C) or heated to the noted temperature and stirred for a given period of time (see Table 1). In the case of the reactions without the sodium hydroxide, the polymer and chloroacetate mixture was heated to reflux for six hours immediately after they were added together. After cooling the pH was adjusted to 7 using hydrochloric acid (J. T. Baker) or sodium hydroxide as necessary. The polymer was recovered under vacuum by either rotoevaporating or freeze-drying, with freeze-drying being the preferred method. The material was dried overnight in a vacuum oven at 60°C and stored in a sealed bottle in a desiccator until needed.

The course of various polymer and chloroacetate reactions was followed by ion chromatography (IC). The samples were treated as follows: approximately 10-mL sample was taken from the reaction vessel at 1-hour intervals starting with the beginning of reflux and the pH determined on a Corning Model 340 pH meter. One milliliter of this was pipetted into a 2-mL volumetric (the rest of the sample being returned to the reaction vessel), the pH adjusted to 7, the solution diluted to the 2-mL mark, the sample transferred to a Centricon 10 (Amicon) concentrator, and centrifuged for one hour at 5000 rpm. The filtrate was diluted 1 to 250 (for a total dilution of 1:500) and analyzed for unreacted chloroacetate and glycolate (a byproduct of chloroacetate). The ion chromatography was performed using a Dionex 2120i chromatograph with an AS11 column, anion self-regenerating suppression (ASRS-I), and conductivity detection at 30 μ Siemens. The gradient employed was 10% 5.0 mM NaOH/ 90% water to 65% 100mM NaOH/ 35% water over 15-minutes at a flow rate of 2-mL/min.

Samples were also sent to Galbraith Laboratories, Inc. for elemental analysis (EA) to confirm the amount of functionalization and to help determine if the polymer was in the acid or sodium salt form. The polymers were analyzed for carbon, hydrogen, nitrogen, sodium, total halogens (calculated as chlorine), and Karl Fischer water.

The viscosity measurements were performed using a Cannon-Fenske size 50 viscometer or Cannon-Ubbelohde size 50 dilution viscometer. Reference solution for the polymer solutions was 1 M LiCl at pH 7. All flow rates were determined in a temperature-controlled water bath at 25°C.

Results and Discussion

Table 1 summarizes the reaction conditions used for the general reaction scheme below:

where **P** represents the polymer backbone. Various conditions were used in an attempt to optimize the functionalization, determine the effects of level of functionalization on the physical and binding properties of the chelating polymer and to compare the capacities.

The reactions were monitored by ion chromatography to determine the absolute amount of reagent incorporated within the backbone polymer. The amount of carboxylate incorporated was calculated from the amount of unreacted chloroacetate and glycolate. Table 1 gives the results calculated from ion chromatographic analysis for the various reaction conditions. As the amount of chloroacetate and sodium hydroxide increased in relation to the polymer the overall percent of incorporation of carboxylate on the polymer decreased, while the absolute amount of incorporation increased. This could be due to a number of things: (1) the competing reaction of chloroacetate with NaOH converting the chloroacetate to glycolate, which would tend to have greater consequence as the amount of each was increased; (2) as the amount of chloroacetate to available nitrogens on the polymer increases so does the hindrance at these sites, which would tend to decrease the functionalization rate and amount. The number of carboxylates incorporated into the polymer will eventually be limited by the total number of nitrogens available for functionalization. Therefore, no matter how much the chloroacetate ratio is

increased, the incorporation will level off. This can be seen in Figure 1 from a plot of carboxylate used versus actual carboxylate incorporated onto the polymer.

It should be noted that the calculations can also be repeated using the elemental analysis data to determine the amount of ligand incorporation. From the elemental analysis data it was determined that the functionalized polymers were in the acid form since the sodium content was low (<5%). Using the elemental analysis data and a graph of functionalization versus C:N ratio (Figure 2), the amount of functionalization was calculated from the C:N ratio. Table 1 gives a comparison of the data obtained from the ion chromatography method and elemental analysis.

As can be seen from Table 1, the data are in good agreement between the two methods, though the elemental analysis results tend to give higher overall values for the amount of functionalization. Figure 1 gives a graph of carboxylate used versus equivalents used from the elemental analysis data. The two methods are very close to about the half functionalized level, but diverge some at the higher levels. This likely come from the error in an indirect determination in measuring large amounts of unreacted chloroacetate (or glycolate) using the IC method as would be present for these high ratios of reagents. Figure 1 can be used for predicting the amount of functionalization a given amount of chloroacetate would give.

The data from the reactions in Table 1 give a functionalization of 0.42 for sample 4 and 0.55 for sample 6. This tells us that 42% if the available nitrogen sites are functionalized for sample 4 and 55% of the available sites are functionalized for sample 6. When repeated on a larger scale starting with 150 grams of polymer the reactions gave the following functionalizations: 0.43 and 0.585, respectively, both in good agreement with the small scale data. Thus, scaling the reaction maintains the ratios of functionalization.

The functionalization data can also be used to help calculate the theoretical yields for the reactions and from there the percent incorporation and weight percent yields can be determined. It should be noted that while the functionalization for the reactions without sodium hydroxide are equivalent or higher in percent incorporation of carboxylate to those with sodium hydroxide, the one example shows the weight percent yield to be lower. As yet no explanation can be offered for this difference.

The viscosity (from concentration versus inherent viscosity) versus functionalization (determined from elemental analysis and C:N ratio) data is shown in Figure 3. The viscosities were all determined at pH 7.0 in 1.0 M LiCl. The viscosities for all the functionalized polymers are less than the base polymer. But there does not appear to be any linear correlation between viscosity and level of functionalization. It is

interesting that though the absolute incorporation between P-.5 and P-.75 is not that much different as indicated in Table 1, the physical properties are quite different. The viscosity of P-.5 is substantially less than all the other polymers indicating that it might have a more spherical nature or a smaller hydrodynamic volume. This could possibly be explained from the level of protonation. At pH 7 the molecule may have a near equal amount of positive and negative charges, and thus the molecule will be attracted to itself and thus have a smaller volume.

Binding studies with nickel(II) were performed with the four levels of functionalized polymer (sample Nos. 1, 4, 6, 7, prepared under similar conditions). One can see from Figure 4 that as the functionalization increases the metal binds increasing stronger at lower pH values. Though the two curves for P-.50 and P-.75 materials appear to have similar binding, the P-.75 material had some precipitation at lower pH values as did the P-1.0 material. As the amount of carboxylate nature of the polymer increases it is a better nickel binder. This could be that there are more aminodicarboxylate sites present, which give more preorganization, thus higher metal-binding constants. The pH dependency curves show a wide range of metal binding ability, which could be useful for selective metal-removal from mixtures.

The capacity for protons for these polymers is about 6.3 ± 0.4 meq/g. This compares favorably with Bio-Rad's Chelex 100 at 2 meq/g.

Conclusions

Form this work we can see that even though the same backbone polymer has been functionalized with the same carboxylate group, that indeed we have four very different polymers in respect to both their binding properties and physical properties. We have shown that, when the level of functionalization exceeds 45%, the polymers have poorer solubility at lower pH values. We also observe a large difference in the viscosities from the higher functionalized material to the lower functionalized material. It was thought that viscosity measurement might be useful as a quality control for large scale synthesis of the polymer, but it is not clear what the structure of the curve means. At present it would seem that elemental analysis might be the quickest and easiest method for determining the functionalization of the polymers.

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Table 1. Compounds, conditions and yields for carboxylation.

No.	Reagents Used	Reaction Conditions	Theoretical Function-alization	Function-alization from IC (% incorporated)	Function-alization from EA	% Yield from EA
1	Polymer* 10 g Na chloroacetate (0.058 eq) Na hydroxide (0.060 eq)	Refluxed for 3 hours, 94°C	0.25	0.22(87.8%)	0.23	112
2	Polymer 10 g Na chloroacetate (0.116 eq) Na hydroxide (0.117 eq)	Stirred for 24 hours, 50°C	0.66	0.49(74.8%)	not determined	78.8 from IC
3	Polymer 10 g Na chloroacetate (0.116 eq) Na hydroxide (0.117 eq)	Stirred for 5 hours, 50°C	0.66	0.37(56.3%)	0.41	82.6
4	Polymer 10 g Na chloroacetate (0.116 eq) Na hydroxide (0.117 eq)	Refluxed for 4.5 hours, 94°C	0.50	0.42(84.1%)	0.42	83.1
5	Polymer 10 g Na chloroacetate (0.116 eq)	Refluxed for 6 hours, 94°C	0.50	0.48(95.4%)	0.48	78.5
6	Polymer 10 g Na chloroacetate (0.174 eq) Sodium hydroxide (.1741 eq)	Refluxed for 3 hrs 8 min, 94°C	0.75	0.55(73.4%)	0.58	87.0
7	Polymer 10 g Na chloroacetate (0.233 q) Na hydroxide (0.233 eq)	Refluxed for 3 hours, 95°C	1.00	0.63(63.4%)	0.71	88.5
8	Polymer 10 g Na chloroacetate (0.232 eq)	Refluxed for 6 hours, 94°C	1.00	0.62(62.4%)	0.62	59.4

*An equivalent weight or unit is considered to be 43.1 g/mole

Figure 1. Carboxylate used versus actual carboxylate incorporated. Data from ion chromatography and elemental analysis.

Figure 2. Theoretical functionalization versus carbon:nitrogen ratio.

Figure 3. Actual functionalization versus intrinsic viscosity

Figure 4. Release curve for nickel with 4000 ppm of polymer, 300 ppm Ni(II), 25 ppm Cr(III) in 0.1 M Na₂SO₄.