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Enhanced Ionic Recognition by Polymer-Supported Reagents: Synthesis and Characterization of Ion-Exchange/Precipitation Resins

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ABSTRACT: A new bifunctional resin is introduced with enhanced ionic recognition for targeted metal ions. The resin operates through both ion-exchange and precipitation reactions and forms the third class of the dual mechanism bifunctional polymers. The polystyrene-based resin consists of phosphonic acid groups for the cation-exchange reaction and quaternary amine groups whose associated anion is responsible for the specific precipitation reaction. Changing the associated anion from hard to soft allows for control of the ionic recognition process. Under identical conditions, the bifunctional trimethylamine/acid resin with the sulfate ion as the associated anion absorbs 92.8% of the barium in solution compared to 27.3% of the calcium. Enhanced ionic recognition for barium arises from barium sulfate precipitation. Changing the associated anion from sulfate to thiocyanate or iodate leads to different metal ion selectivities. The trimethylamine/acid resin with the thiocyanate counterion absorbs 68.4% of the silver ions in solution after a 1-h contact which is also what is calculated to occur on the basis of the monofunctional resin performance, thus indicating that the cation- and anion-exchange mechanisms are operating independently. Bifunctional group cooperativity is evident with the tributylamine/acid resin in the thiocyanate form since 40% of the silver is absorbed from solution in 1 h compared to 26% based on the monofunctional resin performance, while 70.5% is absorbed in 17 h compared to an expected 36%. The same resin in the iodate form absorbs 68.0% of the lead ions in solution at 5 min while 38% absorption would be expected. The phenomenon whereby more metal ions are absorbed from solution when two ligands are on a bifunctional resin than would be expected from the monofunctional resin results is termed polymer-supported synergistic extraction. A high level of ionic recognition with polymer-supported reagents is thus seen to depend upon their ability to operate by an *access mechanism* (such as ion exchange) and a *recognition mechanism* (such as reduction, coordination, or precipitation).

Introduction

The use of polymer-supported reagents to selectively remove one component from a multicomponent solution is important in many applications from metal ion separations[1] to bioseparations.[2] The selective complexation of metal ions, in particular, has been the focus of much research within the fields of catalysis,[3] ion chromatography,[4] and metal ion recovery processes.[5] Specificity in the polymeric ligand to metal ion interaction is critical to the design of stable polymer-supported metal catalysts which do not lose their activity through loss of the metal into the reacting phase. Ion chromatography relies upon different degrees of specificity in order to achieve separation and identification of metal ions. Lastly, metal ion recovery processes require a high degree of specificity in the polymer-supported reagent for gold, mercury, silver, etc. Such processes involve targeted metal ions whose recovery from the aqueous environment is economically important,[6] strategically important,[7] or environmentally important.[8] In each case, the targeted metal ion to be separated is usually a minor component in a solution containing many other ions.

Metal ion recovery processes often employ liquid organophilic extractants for selective separations.[9] Such extractants, usually dissolved in an organic solvent, are contacted with the aqueous solution and remove the metal ion through ion-exchange and/or coordination mechanisms.[10-13] Extractant losses into the aqueous phase can be a significant problem and occur due to their aqueous solubility as well as due to entrainment where emulsified droplets in the aqueous phase are discarded because of the inordinate amount of time required for full phase disengagement.[14]

Polymer-supported extractants offer an ideal alternative to liquid extractants because of their long-term stability and ease of continuous operation. Ion-exchange resins of the strong and weak acid type are the most readily available polymeric metal ion complexing agents but they are not generally applicable.[15,16] Many polymer-supported extractants have thus been prepared with the ultimate goal

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of selectivity; e.g., polymeric tetraazacyclotetradecane is selective for Cu^{II},[17] polymeric dipyridylamine is selective for Fe^{III},[18] and polymeric hexyl thioglycolate shows selectivity for Ag^{I}.[19] While being important contributions to the understanding of polymer–metal selectivities, many such extractants are difficult to prepare in large quantities due to the required sequence of reactions.

The purpose of this research is to synthesize a series of polymers with an enhanced ability for molecular and ionic recognition due to the presence of very specific reacting ligands. These polymers can be applied to the selective separation of metal ions, small organic molecules, and biopolymers from aqueous solutions through readily controllable electrostatic interactions. A new category of resins, *dual mechanism bifunctional polymers* (DMBP's),[20] has thus been introduced. Metal ion separations have been the focus of continuing studies to date. An understanding of the polymer-to-metal electrostatic interactions is critical to the design of polymers which will effectively complex and separate polar molecules including biopolymers. Metal ion reactions, then, remain the topic of the current report but an extrapolation to biomolecular separations is presented.

The DMBP's remove metal ions from solution by two mechanisms via two different functional groups on a given support structure. One mechanism is ion exchange since this enhances the accessibility of the polymer to the metal ion; a reaction then occurs along with ion exchange which enhances the selectivity of the polymer to certain metal ions. The phosphorus acid ligand (phosphinic acid or phosphonic acid) has been the ion-exchange ligand of choice because of its inherently greater selectivity than the sulfonic acid ligand and stronger acidity than the carboxylic acid ligand. The first class of resins within the DMBP category superimpose a redox mechanism upon the ion-exchange reaction.[20] The ion-exchange/redox resins have a very high selectivity for mercury and are able to yield the pure metal from a solution of its ions with the nonacidic P–H bond of a primary phosphinic acid serving as the reducing agent. The second class of DMBP's superimpose a coordinative mechanism upon the ion-exchange reaction.[21] These ion-exchange/coordination resins utilize a phosphonic acid group for the former mechanism and either a tertiary amine or a phosphonate ester group for the latter.

This report introduces the third class of DMBP's, the ion-exchange/precipitation resins. Specificity for targeted metal ions with these polymers is due to the precipitation reaction which occurs (ideally) within the resin bead after ion-exchange occurs. The two ligands on the polymer support are the phosphonic acid ligand for ion exchange and the quaternary amine ligand through which precipitation occurs via its associated anion and the ion-exchanged metal. Given, then, a bifunctional resin having the quaternary amine associated with a chloride ion and contacting a Ag^{I} solution, it is anticipated that cation exchange will occur first bringing the Ag^{I} into the resin followed by AgCl precipitation within the bead. Specificity for one ion, or group of ions, within the solution can be achieved by proper choice of the associated anion.

The ion-exchange/precipitation resins proposed here should lead to both specificity of metal ion removal from aqueous solutions and ease of metal ion recovery.[22,23] The aim is to design resins which perform via intraresin precipitation thus isolating the precipitate within the bead. The metal could then be recovered by solubilizing it through adjustment of the aqueous phase eluent parameters (pH, temperature, etc.). The possibility that clogging of the resin micropores would occur will be monitored through the percent metal absorbed from solution under batch conditions. Adjusting the polymer microporosity (through the cross-link level) and the macroporosity over a wide range may prove to be important to the rate of metal removal and ease of metal recovery. Adjusting the amine's associated anion will be critical to the specificity of the polymer-to-metal ion reaction.

In a broader sense, this study examines the electrostatic interactions both within the resin and in the resin-to-metal reaction. An understanding of the mechanism by which a polymeric reagent recognizes a target polar/ionic species and follows this "ionic recognition" with a highly specific reaction leading to the target's separation from the aqueous solution is very important to the design of polymers for specific biomolecular separations through ionic interactions.

Experimental Section

The synthesis of the poly(vinylbenzyl chloride) support via suspension polymerization has been detailed.[24] The copolymer consists of 96.4% by weight vinylbenzyl chloride, 2.00% divinylbenzene as the cross-linking agent, and 1.60% ethylvinylbenzene (originally present in the divinylbenzene solution). The partial and complete functionalization reactions to the phosphonic acid resin have also been detailed.[21]

Each elution noted below with different solutions is over a 1-h time period unless otherwise noted.

Trimethylamine/Phosphonic Acid Resin. Partially functionalized phosphonic acid resin in the sodium salt form (55 g dry weight) in a 2-L three-neck round-bottom flask equipped with an overhead stirrer, condenser, and thermometer is refluxed with 1 L of 25 wt % aqueous trimethylamine (Aldrich) for 4 h. The resin is conditioned with 1-L elutions of water, 1 N NaOH, water, 1 N HCl, and water.

Trimethylamine Resin. The trimethylamine resin is prepared in the same manner as the amine/phosphonic acid resin above except that amination is carried out on poly(vinylbenzyl chloride) beads. The elution sequence is as above with the amine/acid resin.

Tributylamine/Phosphonic Acid Resin. The sodium salt form of the partially functionalized phosphonic acid resin (12.5 g dry weight) is eluted with 1 L of 95% ethanol and placed in a 500-mL three-neck round-bottom flask equipped with an overhead stirrer, condenser, and thermometer. It is refluxed with 268 mL of 80 vol % tributylamine (Aldrich) in dry dioxane for 18 h. The resin is then conditioned with successive elutions of 1 L of 95% ethanol, water, 1 N NaOH, water, 1 N HCl, and water.

Tributylamine Resin. The tributylamine resin is prepared in the same manner as the amine/phosphonic acid resin except that it is the poly(vinylbenzyl chloride) beads that are aminated. The elution sequence also remains the same.

Determination of the Amine and Phosphorus Capacities. The amine capacity is determined by eluting the resin in its chloride form with 1 L of 4 wt % $NaNO_3$ and analyzing the eluent for chloride ion by Mohr titration.[21] The anion-exchange capacity thus obtained was confirmed by chlorine elemental analyses on the dried resin in its chloride and nitrate forms. The phosphorus capacity is determined via elemental analysis.[24]

Conversion of the Amine Ligand to the Sulfate, Thiocyanate, and Iodate Forms. The amine/acid and the pure amine resins are converted from the chloride to the sulfate form by elution with 1 L of 1 N sulfuric acid followed by 1 L of water. They are converted to their thiocyanate forms by elution with 1 L of 1 N KSCN followed by 1 L of water. They are converted to their iodate form by elution with 2 L over a 2-h period of a saturated potassium iodate solution (approximately 0.2 N) followed by a 1-L water elution.

Barium and Calcium Extraction Studies. The barium and calcium extraction studies are set up with an initial ratio (R_i) of milliequivalents of metal ions to milliequivalents of phosphorus and/or amine sites of 0.5, 1.0, and 1.5. A given weight of resin is then contacted with 50 mL of 0.005 N, 0.010 N, and 0.015 N standard aqueous barium or calcium nitrate solution and shaken on a Burrell wrist-action shaker for 5 min, 1 h, 3 h, or 6 h. The

Table I
Percent Ca and Percent Ba Absorbed from Solution for Monofunctional and Bifunctional Resins with Sulfate as the Resin Anion

		Ca			Ba		
R_i	time, min	acid	amine	amine/acid	acid	amine	amine/acid
0.5	5				44.9	72.2	66.1
	60	47.1	0	26.9	46.1	82.5	89.5
	180	48.1	0	27.3	45.3	85.4	92.8
1.0	60	26.4	0	13.0	25.5	82.1	70.0
	180				27.5	86.1	70.4
1.5	60	23.5	3.5	13.0	18.7	47.6	44.8
	180				18.8	64.3	48.4
	240				19.7	69.5	49.2

amount of barium or calcium remaining in solution was determined by EDTA titration.

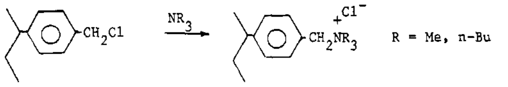
Silver and Lead Extraction Studies. The silver and lead ion extraction studies are set up at an initial ratio of 1 mequiv of metal ions to 1 mequiv of phosphorus and/or amine sites on the resin. An appropriate weight of resin is thus contacted with 100 mL of approximately 0.01 N standard aqueous metal nitrate solution and shaken on a Burrell wrist-action shaker for a set period of time.

The amount of silver remaining in solution after contact with the resin is determined by a Volhard titration.[20]

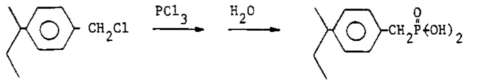
The amount of lead remaining in solution is determined by an EDTA titration using Eriochrome-T as the indicator.

Results and Discussion

The monofunctional and bifunctional quaternary amine resins were initially studied with trimethylammonium ligands. The syntheses of the amine, acid, and amine/acid resins are given in eq 1–3. The monofunctional amine resin had a total anion-exchange capacity of 4.33 mequiv/g, the monofunctional acid resin had a phosphorus capacity of 3.57 mequiv/g, and the bifunctional resin had an amine capacity of 2.64 mequiv/g plus a phosphorus capacity of 1.85 mequiv/g.



(1)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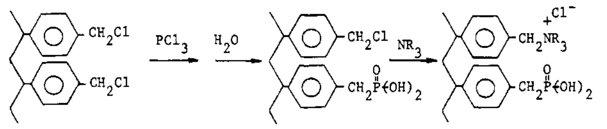
(3)

Anion exchange on both resins with quaternary amine sites is readily accomplished by elution with the appropriate acid or salt. Given that calcium and barium were the first ions whose removal from aqueous solution was to be quantified, each resin was eluted with 1 L of 1 N H_2SO_4 in order to convert the resins to the sulfate form. The ability of the resins to distinguish between barium and calcium was then studied through sulfate salt formation.[25] The percent metal absorbed from solution as a function of time at different initial ratios (R_i) of milliequivalents of metal in solution to total milliequivalents of resin exchange sites (amine and/or phosphorus) is given in Table I. Cation exchange with the acid resin reaches equilibrium in less than 1 h and probably occurs within 5 min. Additionally, the monofunctional acid resin cannot distinguish between calcium and barium given that it absorbs an identical level of both ions. The monofunctional amine resin, on the other hand, removes barium from solution through barium sulfate precipitation: anion exchange occurs between the resin sulfate anion and the solution nitrate ion leading to the solution precipitation. Equilibrium is reached within 1 h except at the highest R_i. Clogging of the resin micropores is not a problem given the very high level of barium removal; at an R_i of 1.5, 100% anion exchange would yield 67% barium removal from solution as found within experimental error. The amount of calcium in the solution contacting the amine resin remains almost constant given the solubility of $CaSO_4$. The performance of the bifunctional resin is a mix of the acid and amine resin properties. Calcium removal reaches equilibrium within 1-h contact time and occurs via the cation-exchange mechanism. Barium removal reaches equilibrium in 1 h in each case, undoubtedly through both the cation- and anion-exchange mechanisms. It is probable that each mechanism is operating independently: the amount of metal absorbed by the bifunctional resin is similar to what one would expect on the basis of the performance of the monofunctional resins (vide infra). Comparison of the performance of the amine/acid resin with the monofunctional amine and acid resins allows a determination of the relative importance of the anion- and cation-exchange mechanisms. A much greater level of absorption by the bifunctional resin than anticipated by the performance of the monofunctional resins must then be due to cooperation between the two functional groups when on the same support network. This concept is explored further in the next set of resins to be synthesized.

Table II
Percent Ag Absorbed as a Function of Contact Time for Monofunctional Amine Resins

	5 min	1 h	6 h	17 h	24 h
CH_2NMe_3/Cl	89.5	98.8			98.5
CH_2NMe_3/SCN	37.4	85.3			98.3
CH_2NBu_3/Cl	17.3	76.1			98.7
CH_2NBu_3/SCN	2.4	4.6	23.7	25.6	

A less hydrophilic resin anion would be expected to show a decreased tendency to ion exchange with the solution anion, especially if the amine R group displayed a greater organophilicity relative to the methyl group. A bifunctional resin with the tributylamine moiety was thus synthesized since it would be expected to display different affinities to the various resin anions relative to the trimethylamine moiety. The amine resin (eq 1, R = *n*-Bu) had a total anion-exchange capacity of 1.85 mequiv/g while the bifunctional resin (eq 3, R = *n*-Bu) had an anion-exchange capacity of 1.47 mequiv/g and a phosphorus capacity of 1.88 mequiv/g.

The thiocyanate anion is a soft, polarizable anion which would be expected to be less hydrophilic than the much harder sulfate anion.[26] It forms insoluble salts with copper, silver, lead, and mercury and thus could be used for their recovery from aqueous solutions. Additionally, thiocyanate is a good test of the hypothesis that a less hydrophilic anion should prefer to stay on a more organophilic support rather than exchange into solution. The amine and amine/acid resins were therefore converted to the thiocyanate form by eluting with 1 L of 1 N KSCN. The acid resin was also eluted with the KSCN in order to put the phosphonic acid ligand in the same form as it would be found in the amine/acid resin. Each resin was shaken for a given period of time with enough solution to give 1 mequiv of Ag^+/mequiv of exchange sites on the resin. The percent silver absorbed from solution was determined titrimetrically. A comparative study of monofunctional amine resins in the thiocyanate and chloride forms is given in Table II. The tributylamine resin was compared with the trimethylamine

Table III
Percent Ag Absorbed as a Function of Contact Time for Monofunctional and Bifunctional Resins with Thiocyanate as the Resin Anion

	5 min	1 h	6 h	17 h	24 h
acid	43.4	44.0			43.7
CH_2NMe_3SCN	37.4	85.3			98.3
CH_2NMe_3SCN/acid	43.7	68.4			71.7
CH_2NBu_3SCN	2.4	4.6	23.7	25.6	
CH_2NBu_3SCN + acid	28.3	31.6	34.7	44.5	44.7
CH_2NBu_3SCN/acid	32.5	40.3	55.5	70.5	67.6

resin. Both resins remove silver ions from solution via anion exchange followed by solution precipitation and provide a quantitative measure of the exchangeability of anions of different polarizability/hydrophilicity as a function of ligand organophilicity. The results show that trimethylamine resin/chloride–solution/nitrate anion exchange, driven by silver chloride precipitation, goes to completion within 10 min. Given the essentially quantitative recovery of silver which occurs, it is important to note that the ion exchange + precipitation reaction does not necessarily lead to clogging of the resin; the behavior of more highly cross-linked (and thus diminished microporosity) resin is currently being studied. Changing the resin anion to thiocyanate on the trimethylamine resin ligand results in a lower rate of anion exchange, though near-quantitative recovery is still achieved. The resin ligand has a pronounced effect on the rate of exchange: chloride–nitrate exchange is five times slower in the tributylamine resin relative to the trimethylamine resin at the shortest contact times, though the gap closes considerably at 1-h contact and is nonexistent at equilibrium. Again, the near-quantitative silver recovery points to an absence of clogging even with this less hydrophilic resin. The effect of combining a more organophilic ligand (NBu_3) with a less hydrophilic anion (SCN^-) is seen in the last entry of Table II. It is clear that the soft, polarizable thiocyanate ion much prefers the tributylammonium ligand over the aqueous solution given that the anion exchange is almost negligible at a 1-h or less contact time. The final value attained is also much less than the quantitative recovery found with the other resins. Anion exchange is thus greatly slowed by proper choice of the resin ligand/anion pair. The results are temperature dependent: at 1-h contact time, the NBu_3/SCN resin shows 12.8% silver absorbed from solution at 40 °C and 19.9% at 60 °C. Increasing the contact temperature from 25 to 60 °C does not approach the recovery possible with the NMe_3/SCN resin and points to the strong organophilic interaction between the NBu_3/SCN ion pair. The effect of this interaction on the reaction mechanism of the amine/acid bifunctional resin was also studied.

The performance of the bifunctional resins in silver recovery is compared to that of the monofunctional resins in Table III. The bifunctional trimethylamine/acid resin has an amine capacity of 2.64 mequiv/g (59% of the total capacity) and a phosphorus capacity of 1.85 mequiv/g (41% of the total capacity). The bifunctional tributylamine/acid resin has an amine capacity of 1.47 mequiv/g (44% of the total) and a phosphorus capacity of 1.88 mequiv/g (56% of the total). The monofunctional acid resin reaches equilibrium within 5 min, as expected, given that pure ion exchange is diffusion controlled, and the trimethylamine–thiocyanate resin probably reaches equilibrium within 2 h. The bifunctional resin mirrors the performance of the individual monofunctional resins. The percent Ag absorbed for the trimethylamine/acid resin is what would be expected given the monofunctional resin results: if it is assumed that the amount of silver removed from solution is dependent only on the resin ligand concentration (it actually is dependent on the ratio of the metal ion solution concentration to the resin ligand concentration, but it is a reasonable approximation at a ratio greater than 0.5),[27] then we calculate a bifunctional resin performance of 40% Ag absorbed at 5-min contact, 68% Ag absorbed at 1 h, and 76% Ag absorbed at 24 h. That the calculated values so closely follow the experimental values leads to the conclusion that, with the trimethylamine/acid resin, the two ligands are acting independently via cation-exchange/anion-exchange mechanisms.

Results obtained with the tributylamine/acid resin contrast with the trimethylamine/acid results. As noted earlier, the tributylamine–thiocyanate removes silver from solution at a very slow rate and never approaches quantitative recovery. The bifunctional resin, on the other hand, removes much more silver from solution (last entry, Table III) than would be expected on the basis of the monofunctional resin results. Calculating the bifunctional resin performance from the monofunctional results leads to percent Ag absorbed values of 25%, 26%, 35%, 36%, and 36% for each of the times indicated in Table III. Whereas the calculated and experimental values were in close agreement with the trimethylamine/acid resin, they are found to be much higher experimentally with the tributylamine/acid resin, indicating bifunctional group cooperativity in the ion-exchange/precipitation reactions. The case for bifunctional group cooperativity is considerably strengthened by simply combining the monofunctional resins in the ratio found with the bifunctional resin and contacting the mixed-resin bed with the silver solution. As seen in Table III (the penultimate entry), the mixed resins perform at a much lower level than the bifunctional resin. Given that the only difference between the mixed resins and the bifunctional resin is the ability of the ligands to cooperate, the higher performance of the latter resin can be ascribed to cooperativity. The mixed resins yield results which are close to the calculated values, at least to 6 h; that they end up somewhat higher than the calculated values (45% versus 36% Ag absorbed) may be due to the higher metal/amine ligand ratio present with the mixed resins which forces the reaction further toward the precipitate. This was not seen with the trimethylamine/acid resin because of the rapid rate of reaction and the quantitative recovery found. It is important to note that much less precipitate is evident with the bifunctional resin than with the mixed resins or the monofunctional amine resin. It is proposed that the major route for a bifunctional resin with organophilic amine moieties supporting less hydrophilic anions is cation exchange first followed by intraresin precipitation. Bifunctionality, then, offers the key advantage of rapid reaction rates when compared to the mixed resin bed performance. The overall rate of reaction (as measured by the percent Ag absorbed from solution) is slower with the tributylamine/acid resin than with the trimethylamine/acid resin where both cation exchange and anion exchange are occurring simultaneously. Even that, however, is not a serious disadvantage, because increasing the temperature decreases the time to equilibrium: at 60 °C and 1-h contact time, the tributylamine–SCN resin absorbs 19.9% Ag, the mixed-resin bed absorbs 42.3% Ag, and the bifunctional resin absorbs 70.8% Ag—which is also its room temperature equilibrium value reached after approximately 12 h.

The kinetics displayed by the bifunctional resin are dependent upon the resin anion and the solution cation: because the tributylamine/acid resin exhibits a slow rate

Table IV
Percent Ag Absorbed as a Function of Contact Time for Monofunctional and Bifunctional Resins with Chloride as the Resin Anion

	5 min	1 h	24 h
acid	31.1	30.7	31.6
CH_2NMe_3Cl	89.5	98.8	98.5
CH_2NMe_3Cl/acid	67.6	68.4	69.6
CH_2NBu_3Cl	17.3	76.1	98.7
CH_2NBu_3Cl/acid	57.7	60.8	60.6

of silver absorption from solution at room temperature when the amine is in its thiocyanate form does not necessarily mean that all silver absorptions will be slow. Table IV details the results for silver absorption with the trimethylamine/acid and tributylamine/acid resins when both are in their chloride form. The operative mechanisms are silver cation exchange and/or AgCl precipitation (K_{sp}(AgCl) 1.56×10^{-10} versus 1.16×10^{-12} for AgSCN).[28] The phosphonic acid resin, both amine resins, and both bifunctional resins were eluted with 1 L of 1 N HCl thus converting all strong base sites to their chloride form and protonating all acid sites. The influence of the resin anion on the kinetics is striking. The trimethylamine mono- and bifunctional resins reach equilibrium within 5–10 min, as opposed to more than 1 h with the thiocyanate anion reaction. The amine and acid ligands are probably acting independently, given that the bifunctional resin's performance can be calculated to be 66%, 70%, and 70% at 5 min, 1 h, and 24 h, respectively, from the monfunctional resins' behavior which is almost identical with the experimental performance. The tributylamine–chloride resin, while slower than the methyl analogue, does reach quantitative recovery eventually, unlike the thiocyanate form of the resin. This indicates an inherently greater affinity of the thiocyanate anion to the tributylamine support. Ligand cooperation enhancing the reaction rate in the bifunctional tributylamine/acid resin is strongly indicated by the fact that equilibrium is attained within 5–10 min and that the calculated performance (25%, 51%, and 61% Ag absorbed at the times indicated) is much lower than found in the short contact times. Thus, the thiocyanate ion reaches a greater level of reaction than expected, though at a relatively slow rate, while the chloride ion reaches the calculated value of reaction at a much greater rate. Both results point to bifunctional cooperativity as an important advantage of the class III resins.

The phenomenon of two polar compounds in an organic solution complexing greater amounts of metal ion in an aqueous solution than the sum of what either one could alone is well-established in solvent extraction chemistry as synergistic extraction.[28] The comparable phenomenon here, brought about by bifunctional group cooperativity, may then be an example of polymer-supported synergistic extraction.

The versatility of the bifunctional ion-exchange/precipitation resins can be illustrated with an example involving the recovery of lead in aqueous solution. When the phosphonic acid, tributylamine, and tributylamine/acid resins after HCl elution are each contacted with lead nitrate solution (at 1 mequiv of Pb^{II}/mequiv exchange sites) for 5 min, the resins absorb 52.2%, 0, and 40.2%, respectively, of the lead in solution. Similar values are obtained at 1-h contact. This, of course, is not surprising due to the solubility of lead chloride. It is possible, then, that a solution of Ag^+ and Pb^{2+} could be passed through the bifunctional resin in its chloride form for recovery of AgCl. Whatever Pb^{2+} went on initially via cation-exchange would probably be displaced off the resin to a large extent as the Ag^+ ions within the resin were depleted as AgCl. If, on the other hand, it was the isolation of lead as an insoluble salt that was targeted, the same bifunctional resin could be used but in an anionic form which would permit the recovery of lead. The iodate anion is a good candidate since lead iodate is an insoluble salt (K_{sp} 2.6×10^{-13}).[29] Eluting the phosphonic, tributylamine, and tributylamine/acid resins with 2 L/2 h of saturated KIO_3 solution and then contacting the resins with lead nitrate solution (1 mequiv of Pb^{II}/mequiv exchange sites) for 5 min yields 61.5%, 7.8%, and 68.0% Pb absorbed from solution for the resins in the order given above. A 24-h contact increases the value for the amine resin only (62.2%, 82.3%, and 72.1% for the resins in the above order). The amine/acid resin thus attains equilibrium in 5 min through bifunctional group cooperativity: note that the calculated performance for the bifunctional resin is 38% after 5 min (68% Pb absorbed, exptl) and 71% after 24 h (72% Pb absorbed, exptl). It would be interesting to determine whether silver ions in a Ag^+/Pb^{2+} mixed solution would precipitate as well at a low contact time given that $AgIO_3$ (K_{sp} 1×10^{-7}) is more soluble than $Pb(IO_3)_2$.

Conclusion

Ion-exchange/precipitation resins have been synthesized and characterized through metal ion recovery experiments. Continuing research into the ion-exchange/precipitation resins includes their performance in multi-ion solutions, the effect of support macroporosity on the kinetics, and the role of temperature in increasing reaction rates. Another very important point to be explored is the extent to which ion exchange and precipitation occur on the bifunctional resin; recovery of the insoluble salt and metal ions in the resin will be critical to this point.

More generally, the initial experiments detailed in this report define the properties required by a polymer-supported reagent in order for it to display bifunctional group cooperativity and a high degree of specificity. The polymeric reagent must be synthesized with the ability to react via two mechanisms, termed the *access mechanism* and the *recognition mechanism.* The access mechanism, ion exchange in this case, serves to bring ions into the polymer network while the recognition mechanism, chosen for its specific reactivity, intervenes once it recognizes the target ion and removes it from solution. This cooperativity allows for greater amounts of the target species to be complexed than the access mechanism could alone, leading to polymer-supported synergistic extraction. If the target is a metal ion and the recognition mechanism is the precipitation reaction, then a relatively hydrophobic associated anion (chosen because of its reactivity with the target ion) is held on the resin by an organophilic quaternary amine site, while a cation-exchange reaction actively brings metal ions into the polymer network. The associated anion then intervenes once the target metal ion comes in close enough proximity to produce an insoluble metal salt, effectively removing the metal from solution. The net effect is an enhanced ionic recognition on the part of the polymer resin for a target species through, in this case, the electrostatic interactions leading to the precipitation reaction.

Electrostatic interactions can also be used to interact differently with different polar moieties thus allowing for enhanced molecular recognition. A primary application would be toward biomolecular separations. Such studies are currently in progress in our laboratory.

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Registry No. KSCN, 333-20-0; H_2SO_4, 7664-93-9; KIO_3, 7758-05-6; Ba, 7440-39-3; Ca, 7440-70-2; Ag, 7440-22-4; Pb, 7439-92-1.

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Oxygen Binding and Transport in the Membrane of Poly[[tetrakis(methacrylamidophenyl)porphinato]cobalt-*co*-hexyl methacrylate]

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ABSTRACT: The copolymer of [α,α′,α″,α‴-*meso*-tetrakis(*o*-methacrylamidophenyl)porphinato]cobalt with hexyl methacrylate (**1**) gives a transparent and flexible membrane. The covalently introduced (porphinato)cobalt reversibly forms its oxygen adduct in the membrane state. Oxygen-binding equilibrium and kinetic constants of the (porphinato)cobalt are much larger than those of the corresponding [α,α′,α″,α‴-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt (**2**) dispersed in the membrane of poly(butyl methacrylate). Oxygen-permeation behavior through the membrane is in accordance with a dual-mode transport model. Ratio of D_C to D_D (D_C and D_D are diffusion coefficients of oxygen via the fixed (porphinato)cobalt and through polymer matrix) is 10 times larger for the copolymer membrane **1** in comparison with that for the dispersed membrane **2**, which indicates effective facilitation in the oxygen transport.

Introduction

A polymer membrane containing a metal complex that interacts specifically and reversibly with molecular oxygen is of great interest as a facilitated transport membrane of oxygen. The authors have recently reported[1-6] that oxygen transport through a poly(alkyl methacrylate) membrane was augmented by the addition of a [α,α′,α″,α‴-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt (CoPP, **2**) complex or a (*N*,*N*′-bis(salicylidene)ethylenediamine)cobalt complex, which forms oxygen adducts rapidly and reversibly even in the solid state. The authors discussed the oxygen permeation profile based on a dual-mode transport model (eq 1).[1-3,7] Here, P is permeability coefficient of

$$P = k_D D_D[1 + FR/(1 + Kp_2)] \qquad (1)$$

$$F = D_C/D_D \qquad R = C'_C K/k_D$$

oxygen, k_D is solubility coefficient of oxygen dissolved in a polymer matrix according to Henry's law, D_C and D_D are diffusion coefficients of oxygen via the complex and through a polymer matrix, C_C' is saturated amount of oxygen reversibly bound to the complex, K is oxygen-binding equilibrium constant, and p_2 is upstream oxygen pressure. The first term of eq 1 represents the permeation for a rubbery polymer membrane, and P is enhanced by the additional second term representing the contribution of the complex.

Four requisites are considered from eq 1 to increase the second term or P: a decrease in p_2, an increase in C_C', large K, and large D_C. In fact, P_{O_2} increases with a decrease in p_2[1-6] and higher concentration of the complex in a membrane brought about higher oxygen permselectivity.[2,3] From the study using the CoPP and

$$M + O_2 \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} M\text{–}O_2 \qquad (2)$$

$$K = k_{on}/k_{off}$$

M = metal ion of the porphinato complex

the FePP complex with various axial, nitrogenous lig-

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