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Dual Mechanism Bifunctional Polymers: Polystyrene-Based Ion-Exchange/Redox Resins

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ABSTRACT: The synthesis of bifunctional phosphinic acid resins that consist of monoaryl (primary) and diaryl (secondary) phosphinic acid ligands supported on a polystyrene network was recently effected. This paper reports that these bifunctional polymers operate by a dual mechanism in that they will ion-exchange with a given metal ion at low pH and then reduce it to its zerovalent state if it has an appropriate reduction potential. The concept of *dual mechanism bifunctional polymers* is thus advanced to describe phosphinic acid resins and their derivatives. The reducing agent is the primary phosphinic acid ligand which becomes oxidized to the phosphonic acid, as shown by analysis with base. The phosphinic acid resins have a high capacity and are stable to prolonged contact with 4 N HNO_3 under ambient conditions. Extraction studies with zinc, mercury, silver, and gold are described. Comparative studies with phosphonic acid, sulfonic acid, and carboxylic acid resins clearly indicate the mechanism of action as well as an extraordinarily high affinity for the transition-metal ions by the phosphinic resins. For example, under very similar conditions, in the presence of excess sodium ions the phosphinic resins absorb 70% of the mercury(II) in solution as opposed to 25% by the sulfonic resins. The phosphinic resins operate by 100% redox of the metal ion absorbed until all of the primary sites are oxidized after which ion exchange occurs.

The complexation of metals to polymer supports yields reagents of tremendous utility. Polymer-supported metal catalysts[1] have been used in reactions as diverse as hydrogenation,[2] epoxidation,[3] hydroformylation,[4] oxidation,[5] and polymerization.[6] Polymer-supported metals have also been successfully applied to chromatographic separations of neutral molecules.[7,8] Polystyrene has proven to be a versatile support due to the large number of ligands that can be covalently bound to it. A judicious choice of ligands can lead to the synthesis of polymer-supported extractants

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that can be used for the recovery of metal ions from aqueous solutions.[9] The recovery of metals such as copper from waste streams is of importance to the hydrometallurgical industry[10] while the recovery of strategic metals such as chromium, palladium, and platinum is of growing national importance.[11]

Significant progress has been accomplished in the bonding of extractant ligands onto polymer supports for the complexation of metal ions.[12] These ligands can be classified as either neutral complexing agents or ionic systems that operate by an ion-exchange mechanism. Polymeric phosphines[4] and polymeric crown ethers[13] provide good examples of coordinating ligands, and polymeric hydroxyoximes[14] are examples of a selective ion-exchange system. Ion-exchange resins available for the complexation of cations include the polystyrene-supported sulfonic acid resins, which are effective under low pH conditions given their highly acidic nature,[15] and the acrylic acid resins, which can form tighter metal complexes due to their weakly acidic nature though at correspondingly higher pH conditions.[16] While polymers containing neutral complexing ligands commonly operate by a coordination mechanism, another type of neutral ligand is that which operates by a redox mechanism: the ligands may contain metal ions, such as ferric complexes, which undergo reduction,[17] or they may be neutral organic moieties such as dihydronicotinamide[18] and hydroquinone[19] which undergo oxidation. Development has been limited due to their hydrophobicity which leads to low apparent rates of reaction.[18]

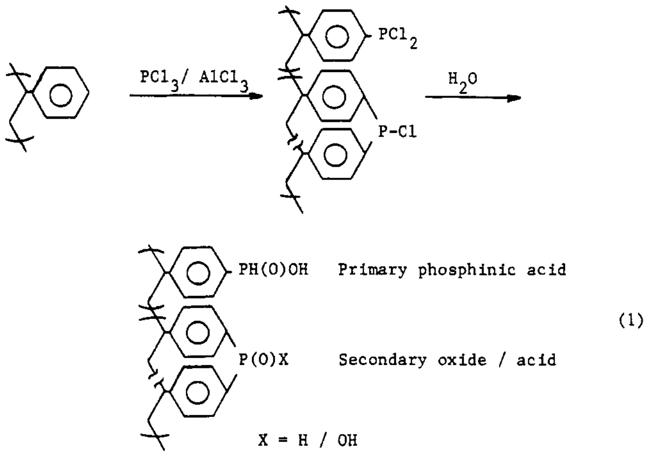
Our research centers on the synthesis of polymer-supported ligands that form tight complexes with metal ions for catalytic applications and yet can ion-exchange in acidic solutions (pH ≤ 1) for use in ion-exchange chromatography and metal ion recovery processes. The synthesis of a stable, high-capacity, hydrophilic polymer that can display different degrees of ion-exchange selectivity for transition-metal ions in solution would offer an important alternative in ion-exchange chromatography to the traditional sulfonic acid stationary phases. Additionally, the ability to reduce metal ions to their atomic state through the ion-exchange ligand would be a significant advance in the recovery of pure metal from dilute solutions. Given these considerations, we have undertaken the synthesis and characterization of phosphorus acid resins with emphasis on the phosphinic acid ligand supported on polystyrene.[20-22] Phosphonic acid resins possess intermediate acidity, making them more selective than the sulfonic acid resins while displaying a much higher capacity than the carboxylic acid resins at low pH.[18] The phosphonic acid resins can be synthesized from the phosphinic acid intermediate through an oxidation reaction using hot concentrated nitric acid,[24] but we have found hydrogen peroxide to work as well; very little emphasis has been placed in the past on the phosphinic acid ligand given that it could be easily converted to the higher capacity phosphonic ligand. It was our objective, though, to synthesize the phosphinic acid resin through a route which would cause the intermediate to disproportionate and allow for the formation of a bifunctional resin upon hydrolysis containing a monoaryl (primary) phosphinic acid ligand and a diaryl (secondary) phosphine oxide ligand (or secondary phosphinic acid depending on the hydrolysis conditions). The differences in ion-exchange selectivities can then be used in both chromatographic separations and metal ion recovery.

We have detailed our synthesis of the phosphinic acid polymers along with proof of the disproportionation reaction[21] as well as a characterization of their selectivity advantage over the sulfonic acid and carboxylic acid resins at low (pH < 1) operating pH.[22] We would now like to detail an additional advantage: high-capacity phosphinic acid resins, stable to ambient conditions, operate by both ion exchange and reduction–oxidation mechanisms through a single, readily synthesized ligand when contacted with an ionic solution allowing for the isolation of zero-valent metal. These resins display a good deal of selectivity, especially with respect to the complexation of transition-metal ions over the alkali-metal ions, and are completely stable to prolonged contact with 4 N HNO$_3$ at room temperature. We propose the term *dual mechanism bifunctional polymers* for the phosphinic acid resins and their derivatives which thus form one specific example of this general class of metal ion complexing agents. We shall be publishing our development of other examples shortly.

Synthesis

Our principal polymer support network is polystyrene, which we synthesize in the form of beads (approximately 1 mm in diameter) by suspension polymerization.[25] The polystyrene network is cross-linked with divinylbenzene (DVB) in order to maintain aqueous phase insolubility after functionalization with hydrophilic substituents. Results presented in this paper deal with 2% and 10% DVB polystyrene beads. The advantage to the lower level of DVB is that it provides for a high-capacity open matrix with no problem of accessibility to the exchanging sites; the advantage to the higher level is that while a lower capacity resin, it is more resistant to attrition without significant accessibility loss. We have established that the same conclusions can be drawn from extraction studies under equilibrium conditions upon the introduction of macroporosity into the support with DVB levels of 10% or less[22] and so detail our results in this paper with non-macroporous (gel) resins.

The functionalization of greatest interest to us is that which leads to the phosphinic acid ligands and has been detailed earlier.[21] High-capacity resins are synthesized by reaction of the polystyrene with PCl$_3$ in the presence of AlCl$_3$ for 4 h at 73 °C followed by hydrolysis. As summarized in eq 1, the 4-h reaction time allows the disproportionation reaction to occur between neighboring interchain and intrachain aryl rings to give a mix of monoaryl dichlorophosphine and diaryl monochlorophosphine ligands. Upon hydrolysis in 1 N NaOH, resin with primary and secondary phosphinic acid ligands is isolated and utilized in the present study. The resin is acid-washed and analyzed with NaOH for total acidity, by phosphorus elemental analysis for total functionalization, and by iodine oxidation to determine the number of primary acid sites.

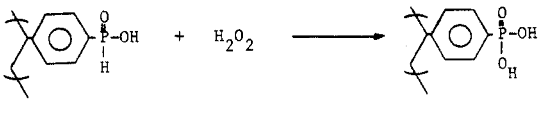


(1)

Analysis of a typical 2% DVB cross-linked phosphinic acid resin used in this study shows it to have a total acid capacity of 4.92 mequiv/g (dry weight) and a total phosphorus capacity of 4.96 mequiv/g, indicating that all phosphorus moieties are acidic and that there is no accessibility problem, since the NaOH analysis is done on whole beads while the elemental analysis is done on resin solubilized with perchloric acid.[21] The iodine oxidation analysis shows that 1.95 mequiv/g of the 4.92-mequiv total consists of primary acid sites, the remaining 2.97 mequiv/g consisting of secondary acid sites. By the use of the same techniques, the 10% DVB cross-linked phosphinic acid resin had the following analysis: 3.90 mequiv/g total acid capacity and 1.81 mequiv/g primary acid capacity (2.09 mequiv/g secondary acid capacity by difference). These data and the comparison with the 2% DVB resin are consistent with results that we have reported.[21]

The phosphinic acid resins are at the center of our metal ion complexation studies. Comparative studies with other ligands are required, though, to fully gauge their unique properties. Consequently, we synthesized polystyrene-supported phosphonic acid, sulfonic acid, and carboxylic acid resins and determined their metal ion extraction abilities. In each case, the initial copolymer was the same in order to ensure constant polymer network effects; thus, we could be certain that any differences in extraction ability were due solely to the chemical nature of the ligand itself. Both 2% and 10% DVB polystyrene beads were used in the synthesis of the phosphonic acid resins, while 10% DVB beads were emphasized with the sulfonic and carboxylic acid resins.

The phosphonic resins, as shown in eq 2, were synthesized from the corresponding phosphinic acid resins by heating with 20% H_2O_2 to 100 °C over a 5-h period and then holding at 100 °C for 1 h. Phosphonic acid resin made from the 2% DVB phosphinic resin had a total acid capacity of 7.04 mequiv/g and that made from the 10% DVB phosphinic resin had a total acid capacity of 5.66 mequiv/g, both in excellent agreement with what would be expected on the basis of complete oxidation of the P–H bond and the sum of the total acid capacity with the total primary acid capacity of the corresponding phosphinic acid resins. More precisely, of course, the phosphonic acid resins are still bifunctional since the secondary phosphinic acid sites retain their integrity through the oxidation.



(2)

The strongly acidic sulfonic resins were synthesized by conventional methodology.[26] Polystyrene beads swollen with 1,2-dichloroethane were reacted with concentrated H_2SO_4 at 130 °C for 3 h. The resin was found to have a total acid capacity of 5.00 mequiv/g.

The weakly acidic carboxylic resins were synthesized by a procedure that we will be detailing shortly. The technique involves reacting 10% DVB cross-linked vinylbenzyl chloride beads that are swollen in toluene with alcoholic KOH at 60 °C for 24 h to allow for full conversion to hydroxymethylene groups. Oxidation with concentrated HNO_3 allows for the formation of carboxylic acid groups without the concomitant nitration of the aromatic rings usually observed. Resin thus synthesized was found to have a total acid capacity of 5.72 mequiv/g.

Metal Ion Analysis: General Procedure

The extraction ability of the resins discussed above for zinc, mercury, silver, and gold ions in aqueous solutions was determined through the use of the corresponding radiotracers (^{65}Zn, ^{203}Hg, ^{110}Ag, and ^{198}Au) with a NaI–TlI well-type scintillation counter. Solutions were made up of varying metal ion concentrations in a constant volume to which a constant weight of resin was added. The amount of metal absorbed from solution was followed by the addition of approximately 0.025 μCi of the metal radiotracer and the loss determined by counting after a 17-h equilibration time. The 17-h equilibration time is overly long, as kinetic studies that we will be publishing indicate,[27] but was maintained simply to ensure equilibrium. Results were correlated as a function of the initial solution concentration (in milliequivalents) per milliequivalent of exchangeable acid sites and reported as the initial ratio, R_i. Batch-to-batch variability in the resin acid capacity from 4.4–5.0 mequiv/g should be considered real, given that it is reproduced by the phosphorus elemental analysis, making normalization via R_i important to comparisons of metal extraction ability among resins. We have thus tabulated, at a given R_i, the percentage resin loading ($(100[M^{n+}]_f)/[\text{available resin sites}]_i$); since the percentage of metal absorbed from solution is a complementary value (% loading/R_i), it has not been explicitly tabulated. R_i levels of 0.01–1.50 have been studied most extensively. The extraction studies were carried out in the presence of a large excess of sodium ions as background (20 mequiv of Na^+/mequiv of acid sites) in order to maintain a fairly constant ionic strength throughout the extraction; for comparison, studies were also done with no sodium present to examine the inherent resin affinity for a given metal ion relative to the hydrogen ion. The pH of the final solution was always approximately 0.5.

While most of our conclusions rely on the radiotracer data, we found that we required another technique for determining the amount of metal taken up by the resin in order to compare with an analysis of the resin itself after the extraction had occurred. For this purpose, we developed a titrimetric technique for the determination of silver (or mercury) uptake based upon the Volhard method.[28] The amount of metal absorbed was analyzed for by titrating a metal nitrate solution with ammonium thiocyanate both before and after resin contact; this amount corresponded to the amount recovered from the resin by elution with nitric acid. As shown below, results obtained by titrimetry were perfectly consistent with the radiotracer results for both silver and mercury.

Results and Discussion

Zinc. Phosphinic acid resins were contacted with zinc ions (from zinc nitrate) in the presence of and in the absence of sodium background; the extraction results under equilibrium conditions with sodium are summarized in Table I. The results in the absence of sodium are illustrated in Figure 1 and depict good ion-exchange behavior. Some advantage to the phosphinic resins over phosphonic resins is indicated by the level of resin loading at a given R_i, which could be ascribed to the somewhat greater acidity of phosphinic acids over phosphonic acids.[29] The importance of acidity is shown in Figures 2 and 3 where 10% DVB cross-linked sulfonic, phosphinic, phosphonic, and carboxylic acids are compared. With no sodium present (Figure 2), the percentage of resin loaded with zinc ions at an R_i of 1 decreased in the order of decreasing ligand acidity (72%, 35%, 22%, 3%, for the sulfonic, phosphinic, phosphonic, and carboxylic ligands, respectively). That acidity is not the only determinant of the usefulness of a resin is shown by the results in the presence of sodium (Figure 3): the percentage of resin loaded at an R_i of 1 became 17%, 25%, 16%, and 4% for the resins as listed

Table I
Extraction of Metal Ions with Phosphorus Acid 2% DVB Resins with Sodium Background

	R_i								
	0.1	0.3	0.5	0.7	0.9	1.0	1.1	1.3	1.5
Zn loading, %									
phosphinic resin	6.51	15.8	20.0	26.0	27.3	28.0	29.2		37.5
phosphonic resin	2.74	7.43	12.6	15.2	18.4	21.0	22.4	25.1	27.0
Hg loading, %									
phosphinic resin	9.98	29.8	49.9	57.1	62.4	69.4	75.6	82.2	91.2
phosphonic resin	8.47	21.5	34.5	43.9	50.6	52.5	56.2	61.8	68.7

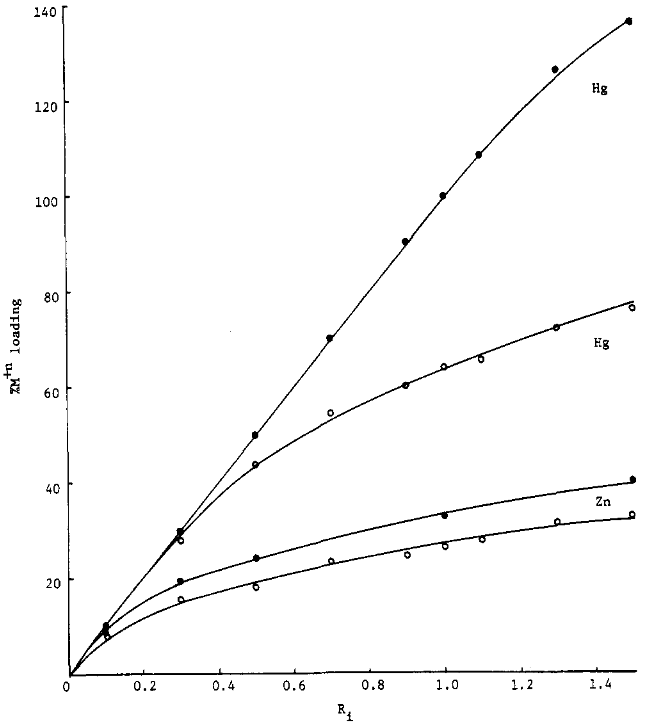


Figure 1. Percentage of M^{n+} loading as a function of R_i for 2% DVB resins with no sodium present: (●) phosphinic; (○) phosphonic.

above, the phosphinic resins being superior at the low pH values (0.5–0.9) studied.

Mercury. Solutions of mercuric nitrate at varying concentrations were contacted for 17 h with the phosphorus acid resins, both with and without sodium ion background, with the aim of defining conditions that would permit a selective absorption of mercury from solution. The results obtained from the radiotracer analysis are presented in Table I (with sodium) and Figure 1 (without sodium) for both phosphorus acid (2% DVB) gel resins. The loading curves without sodium, shown in Figure 1, illustrate two important points. The phosphorus acid resins have a much greater affinity for mercury than they do for zinc, and (noting especially that the resin loads to a value of 136% at an R_i of 1.50) loading values of greater than 100% for the phosphinic acid resins indicate the intervention of a second mechanism in addition to ion exchange. These conclusions remain the same when 10% DVB cross-linked sulfonic acid resin is compared with the phosphorus acid resins. Figure 4 supports our earlier conclusion with zinc solutions that phosphinic acid resin loads to a point independent of cross-link level (at least to 15% DVB)[22] and indicates that mercury loading is greater than 100% only with the phosphinic resin which exceeds even the sulfonic resin loading in the absence of sodium. The phosphorus acid resins thus have a great tendency to absorb mercury, as found by comparing the sulfonic acid with the phosphonic acid results. That a mechanism additional to ion exchange is operative with the phosphinic acid resins may be seen by comparing their results with the phosphonic acid results.

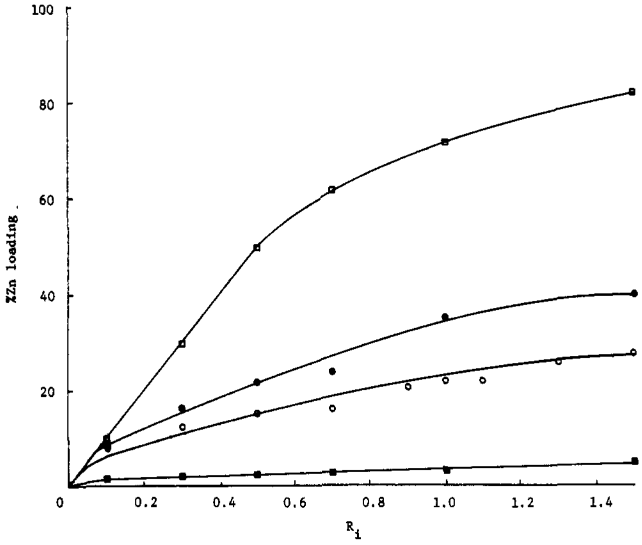


Figure 2. Percentage of Zn loading as a function of R_i for 10% DVB resins with no sodium present: (●) phosphinic; (○) phosphonic; (□) sulfonic; (■) carboxylic.

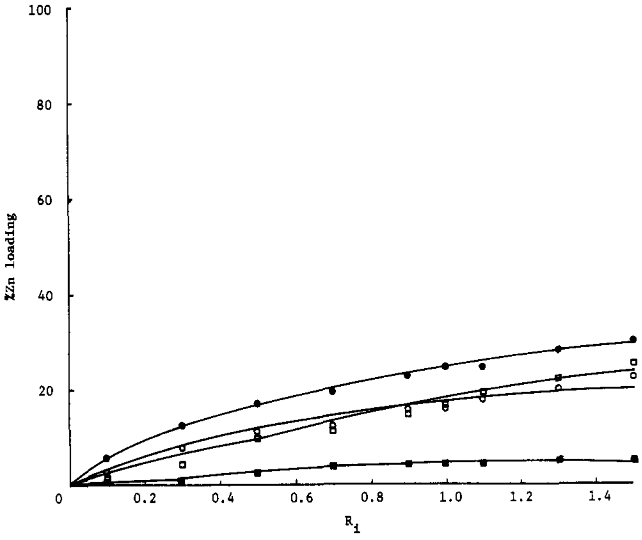


Figure 3. Percentage of Zn loading as a function of R_i for 10% DVB resins with sodium present: (●) phosphinic; (○) phosphonic; (□) sulfonic; (■) carboxylic.

Obtaining more than 100% Hg(II) loading is only one piece of evidence for an additional mechanism. The following observations must also be noted: experiments with 2% DVB cross-linked macroporous resins having 50 vol % porosity showed identical percentages of loading results as those reported for the gel resins; while the gel resins turned a metallic gray after contact with the mercury solution, the macroporous resins were found to produce droplets of metallic mercury on the bottom of the vial, independent of whether sodium was present or not. We

Table II
Extraction of Ag(I) with Phosphorus Acid Resins with Sodium Background

	R_i								
	0.1	0.3	0.5	0.7	0.9	1.0	1.1	1.3	1.5
Ag loading, %									
2% DVB phosphinic	7.01	21.5	37.6	50.3	65.2	68.5	75.1	89.8	97.2
10% DVB phosphinic	6.49	19.5	33.8	46.1	57.6	62.8	66.5	79.0	84.0
2% DVB phosphonic	3.04	10.9	18.0	22.7	26.6	29.9	29.8	36.2	40.3
10% DVB phosphonic	3.31	12.6	18.4	22.5	25.3	28.8	30.8	31.8	32.3

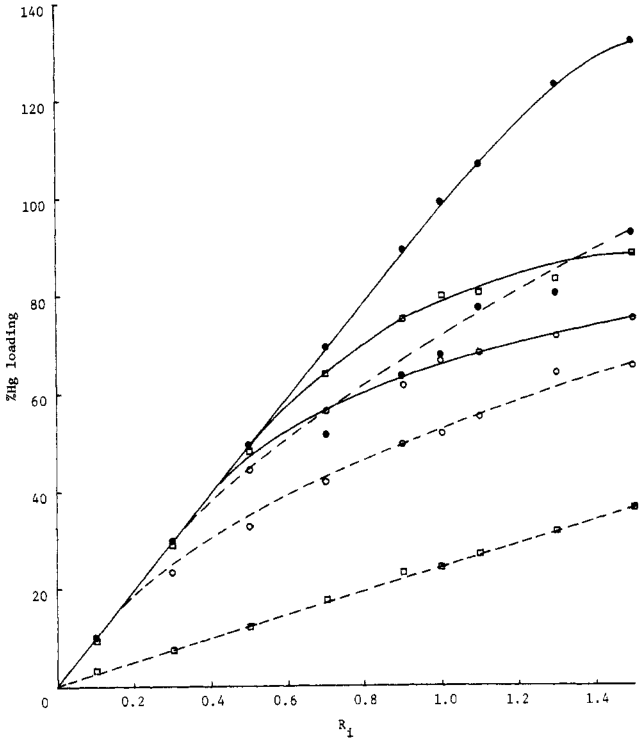
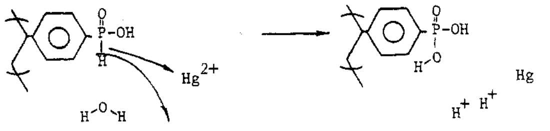


Figure 4. Percentage of Hg loading as a function of R_i for 10% DVB resins with (- - -) and without (—) sodium present: (●) phosphinic; (○) phosphonic; (□) sulfonic.

thus postulate that the mechanism operative in addition to ion exchange is reduction of the metal ions to zerovalent metal with a concomitant oxidation of the phosphinic acid ligand to a phosphonic acid.

The redox reaction, which is probably preceded by ion exchange, is represented in eq 3 with the phosphinic acid



(3)

ligand losing two electrons and the Hg(II) ion gaining two electrons. Standard reduction potential data are consistent with this mechanism since the oxidation potential of H_3PO_2 to H_3PO_3 is +0.50 eV while the reduction potential of Hg(II) to Hg^0 is +0.85 eV.[30]

The redox hypothesis is readily put to the test since it postulates an increase in the acid capacity of the resin through the oxidation half-reaction. We can quantify the extent to which the redox reaction occurs as a function of the amount of mercury absorbed since the mechanism postulates that 2 mequiv of Hg(II) ion will be reduced by 1 mequiv of P-H ligands. In our initial test of the hypothesis, 1 g of phosphinic acid resin having a total acid capacity of 4.39 mequiv/g and a primary acid capacity of 1.83 mequiv/g was contacted with a solution containing 3.42 mequiv Hg(II) ions (R_i = 0.78) and found to absorb 3.40 mequiv/g over a 17-h period; 99.4% of the mercury was thus absorbed from solution, as determined titrimetrically, in excellent agreement with the value of 99.76% interpolated from the radiotracer analysis (equivalent to 77.82% loading, Figure 1). The resin was then eluted with 2 N HNO_3 to remove any ionic mercury and thus regenerate the acid sites. Subsequent analysis of the resin acidity with NaOH showed that it had increased from 4.39 mequiv by 1.89 mequiv to yield a new value of 6.28 mequiv/g. This corresponds to 100% oxidation of the primary acid sites. Given that 3.40 mequiv Hg(II) would oxidize 1.70 mequiv primary acid sites, we can conclude that within experimental error 100% of the mercury which was absorbed underwent reduction. This should be true as long as the amount of mercury absorbed does not exceed the capacity of the primary acid sites. Mercury in excess of that which is involved in the redox process can then be absorbed by the resin via ion exchange.

These conclusions allow us to understand the mechanism by which the resin loading can reach the values observed, as shown by the following experiment. Phosphinic acid resin found to have a total acid capacity of 5.02 mequiv/g and a primary acid capacity of 1.96 mequiv/g was contacted with 14.16 mequiv Hg(II) ions to give an R_i of 2.82. It was found to absorb 9.04 mequiv Hg(II)/g (by radiotracer) for a loading of 180%. Elution with 1 L of 8 N HNO_3 allowed for complete removal of the mercury within the bead by oxidizing the mercury metal to its ionic state and displacing all of the Hg(II) present; a control done with 8 N HNO_3 and phosphinic resin showed no change in resin capacity. The new acid capacity of the now mercury-free resin was then determined to be 7.00 mequiv/g, which is consistent with 100% oxidation of the original 2 mequiv of primary acid sites. The results are also consistent with the extraordinary loading capacity of 9.04 mequiv Hg(II)/g. The 2 mequiv/g of primary acid sites absorb the maximum 4 mequiv Hg(II) by reduction, and the original 5 mequiv of Brønsted acid sites ion-exchange with 5 mequiv Hg(II), thus summing to the observed total.

Silver: Radiotracer Analysis. The focus of the research then became quantifying the extent of redox vs. ion exchange as a function of the initial conditions. The metal chosen for this complete study was silver, rather than mercury, because we found that we could remove better than 90% of the silver absorbed by the beads as either ion or metal by an elution with 1 L of 4 N HNO_3—conditions far less harsh than what nitric acid alone requires to oxidize the beads. The effect of mercury or silver on the resin is probably comparable given that both have very similar reduction potentials (0.85 and 0.80 eV, respectively).[30]

Table II and Figure 5 summarize the Ag(I) extraction data as obtained by radiotracer analysis. In order to allow for comparison with the zinc and mercury data, the percentage of loading is presented as a function of R_i. As with mercury, the percentage of loading on both the 2% DVB and 10% DVB resins exceeds 100% at the higher R_i values, indicating that redox with the metal ion is occurring. When the only process in the resin is ion exchange, defining the initial conditions by the R_i variable that we have

Table III
Recalculation of Ag(I) Extraction Data from Radiotracer Study with 2% DVB Phosphinic Acid Resin as a Function of R_i(total)[a]

	R_i(total)								
	0.064	0.193	0.322	0.450	0.579	0.643	0.708	0.837	0.965
mequiv of Ag absorbed/g	0.433	1.28	2.12	2.92	3.73	4.16	4.56	5.26	5.83
Ag loading, %	6.03	17.8	29.5	40.7	51.9	57.9	63.4	73.2	81.2

[a] No sodium ions in solution.

Table IV
Titrimetric Study of Ag(I) Extraction with 2% DVB Phosphinic Acid Resin as a Function of R_i(total)[a]

	R_i(total)					
	0.053	0.162	0.270	0.373	0.561	1.63
mequiv of Ag absorbed/g	0.458	1.40	2.32	3.31	4.61	8.70
Ag loading, %	5.12	15.7	25.9	37.0	51.5	97.2
theor acid capacity	5.30	5.77	6.23	6.73	7.01	7.01
exptl acid capacity	5.23	5.77	6.19	6.77	7.08	7.18

[a] No sodium ions in solution.

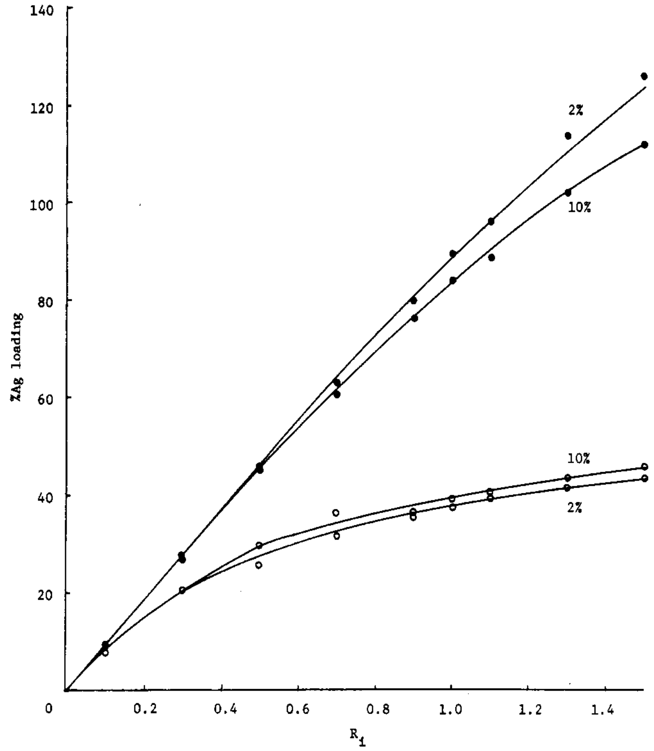


Figure 5. Percentage of Ag loading as a function of R_i for 2% and 10% DVB resins with no sodium present: (●) phosphinic; (○) phosphonic.

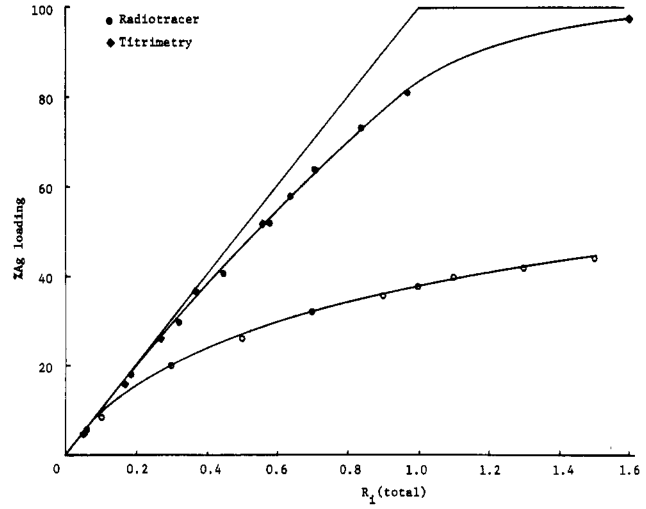


Figure 6. Percentage of Ag(I) loading as a function of R_i(total) for 2% DVB resins with no sodium present: (●) phosphinic; (○) phosphonic.

introduced yields interpretable results; in contrast, when the resin can act by both ion exchange and reduction, the definition of the initial conditions must allow for this total capacity and so we define R_i(total) as the ratio of the initial concentration of metal ion in solution ([mequiv $M^{n+}]_i$) to the initial total capacity of the resin ([mequiv acid capacity]$_i$ + [mequiv electrons available for transfer]$_i$), the former quantity determined by NaOH titration and the latter quantity by twice the value obtained by iodine oxidation. Table III interprets the data from the 2% DVB resin as a function of R_i(total) with Figure 6 illustrating the percentage of loading data; the maximum loading assuming 100% absorption of metal is also indicated along with the loading curve for the phosphonic resin for comparative purposes (R_i(total) = R_i for the phosphonic resins since [mequiv electrons]$_i$ is 0). The recalculation of the data shows that the loading curve does not exceed 100% even when 5.83 mequiv Ag are absorbed per gram of resin (which is greater than the original ion-exchange capacity by 1.2 mequiv/g) because of the additional redox mechanism. Recalculation of the data from the 10% DVB resin shows the same trends as the 2% DVB resin and is not tabulated. Conclusive evidence for the redox process involves an analysis of the resins after metal extraction has occurred as a function of R_i(total) and is presented below.

Silver: Titrimetric Analysis. Titrimetry was undertaken to complement the radiotracer results by allowing for regeneration and analysis of the resins after redox had occurred. Determination of the increase in acid capacity as a function of the amount of metal ion absorbed measures the importance of resin oxidation/metal reduction relative to ion exchange. The resin (total acid capacity = 5.07 mequiv/g, primary acid capacity = 1.94 mequiv/g) was equilibrated with 100-mL $AgNO_3$ solutions of varying normality in order to study a range of R_i(total) levels; the metal (both atomic and ionic) was then eluted from the resin with 1 L of 4 N HNO_3, washed with water, and analyzed for acid capacity. The new acid capacity was compared to the milliequivalent of metal absorbed from solution, allowing the extent of redox to be quantified.

The results in Table IV allow the conclusion that *the phosphinic acid resins operate by 100% redox of the metal ion absorbed until all of the primary phosphinic acid groups are oxidized after which ion exchange occurs.* There is essentially quantitative absorption of the silver

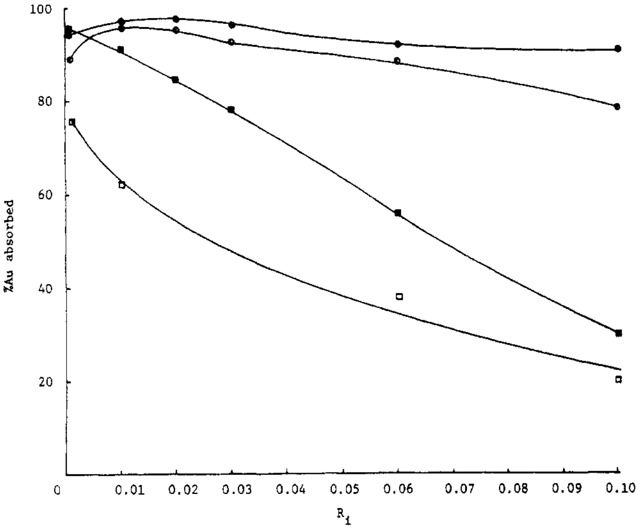
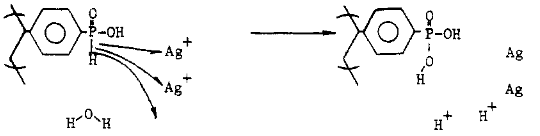


Figure 7. Percentage of Au absorbed from solution in the presence of sodium as a function of R_i for different resins: (●) 2% DVB phosphinic; (◐) 10% DVB phosphinic; (□) 10% DVB sulfonic; (■) 10% DVB carboxylic.

from each solution as long as the redox capacity is not exceeded. The new acid capacity predicted from the milliequivalent of Ag(I) absorbed onto the resin on the assumption of 100% redox and the oxidation of one P–H bond per two Ag(I) ions reduced, as illustrated in eq 4, is



(4)

the capacity experimentally determined. Most importantly, the final acid capacities of the two resins which absorb 4.6 and 8.7 mequiv of Ag(I) are the same, since 3.88 mequiv of Ag(I) is the maximum that can be reduced given the original primary phosphinic acid capacity of 1.94 mequiv/g, with the additional silver being absorbed by ion exchange. The maximum final acid capacity is thus predicted to be 7.01 mequiv/g and is in excellent agreement with the observed values in light of the titration's accuracy to ±0.2 mequiv/g. The excellent agreement between the titrimetric analysis and the radiotracer analysis is best seen in Figure 6 where both sets of data are plotted on the same graph: an approach to 100% loading is clearly indicated as a function of R_i(total).

Gold. Another metal toward which the phosphinic acid resins should have a high affinity is gold. Its reduction potential of 1.42 eV should allow for the facile recovery of metallic gold from very dilute solutions. We have carried out initial experiments dealing with the problem of recovering low concentrations of gold from brine solutions and compared results obtained from the phosphinic acid resins with sulfonic acid and carboxylic acid resins. The percentage of gold absorbed from solutions at various R_i values having 4 N NaCl as background at pH 0.2–0.5 was determined by radiotracer experiments. The results are shown in Figure 7 for 2% DVB and 10% DVB phosphinic resin, 10% DVB sulfonic resin, and 10% DVB carboxylic resin. All of the results are relative to R_i, though it is almost certain that the phosphinic resins are reducing the gold, making R_i(total) more accurate for their absorption results. In any case, the superiority of the phosphinic resin is clearly indicated over the concentration range studied given the nonselective nature of the sulfonic resin with its affinity for the sodium present in great excess relative to the gold and the weakly acidic nature of the carboxylic resin with its affinity for the hydrogen ion at the low pH values studied. Further work with gold recovery is being pursued.

Conclusions

The dual-mechanistic nature of the polystyrene-supported bifunctional phosphinic acid resins that we have synthesized has been established. The primary phosphinic acid ligands reduce all of the metal ions that are absorbed by the resin until they are consumed, after which point ion exchange becomes the principal mechanism of absorption. The resin can be synthesized with primary and secondary phosphinic acid ligands or with primary phosphinic acid/secondary phosphine oxide ligands if additional redox capacity is desired. The lower limit of the reduction potential that the metal ion must possess in order for it to be reduced is still under study. Our current work on the extraction kinetics and the ability to regenerate the phosphinic ligands after the redox process has occurred will be reported shortly.

Experimental Section

All reagents were purchased and used without further purification unless otherwise noted. We have previously reported the synthesis of the copolymer, phosphinic resin, sulfonic resin, carboxylic resin, and the methods of characterization.[21]

Phosphonic Acid Resins. Phosphinic acid resin (10 g dry weight) is placed in a 250-mL round-bottom flask equipped with an overhead stirrer, condenser, and thermometer; 80 mL of 20 wt % H_2O_2 is added and the mixture stirred for 1 h at room temperature. The system is heated over 5 h to 100 °C and held there for 1 h before it is cooled to room temperature.

Metal Ion Analysis by Radiotracer. Each series of vials for a given resin contained a calculated amount of metal ion in a 5-mL solution and enough resin to yield 1 mequiv acid sites. Stock solutions were made up (2 N $Zn(NO_3)_2$, 1 N $Hg(NO_3)_2$, 2 N $AgNO_3$, and 0.075 N $AuCl_3$) in either 2 N $NaNO_3$ or in distilled H_2O. If the loading curves were to be determined in the presence of Na^+, a given amount from one of the $NaNO_3$ stock solutions was used to yield the desired R_i and the remainder of the 5-mL solution consisted of 4 N $NaNO_3$ (4 N NaCl in the case of gold). If the loading curves were to be determined in the absence of Na^+, a given amount from one of the H_2O stock solutions was used to yield the desired R_i with the remaining volume, to 5 mL, taken up by H_2O. Each 5-mL solution contained at least 0.025 μCi of radiotracer cation (^{65}Zn, ^{203}Hg, ^{110}Ag, and ^{198}Au) initially, and the solutions were counted after a 17-h equilibration period. Counting was done in a NaI–TlI well-type scintillation counter using a multichannel analyzer with a region-integrating feature to reduce background interference and increase counting accuracy. One-milliliter samples were counted twice, each for 1 min, and the cpm's averaged for all calculations. Solution pH was measured with a Brinkmann pH meter.

Metal Ion Analysis by Titrimetry. The Volhard method[28] was used in the Ag(I) R_i study; it gave equally good results with Hg(II). In a typical run, 8 g of suction-dried phosphinic resin was placed in a 125-mL bottle with 100 mL of a $AgNO_3$ solution at a concentration appropriate to give the desired R_i. After 17h of shaking a 25-mL aliquot was titrated in order to determine the amount of silver absorbed by the resin with ammonium thiocyanate by using a ferric ammonium sulfate indicator. The new resin acid capacity was then determined by transferring the beads quantitatively to a fritted-glass filter, washing with 1 L of H_2O for 1 h, and then eluting with 1 L of 4 N HNO_3 for an additional hour in order to remove all of the metal from the resin, as checked by a Volhard titration on the eluent. The resin was washed with water until the washings were neutral and the total acid capacity analyzed with NaOH.[21]

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Registry No. Zinc, 7440-66-6; mercury, 7439-97-6; silver, 7440-22-4; gold, 7440-57-5.

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Synthesis, Reactivity, and Role of 4-Vinylbenzyl *N,N*-Diethyldithiocarbamate as a Monomer–Iniferter in Radical Polymerization

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ABSTRACT: For the synthesis and design of graft copolymers through radical polymerization, 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) was prepared and used as a monomer–iniferter (initiator–transfer agent–terminator) which has two functions as a monomer and a photoiniferter. In the absence of light, VBDC polymerized easily with 2,2′-azobis(isobutyronitrile) via an ordinary radical polymerization mechanism, and its reactivity was similar to that of styrene (St). The homopolymer of VBDC and its copolymers with St were found to act as excellent photoiniferter of living radical polymerization in a homogeneous system to give graft copolymers consisting of benzene-soluble and -insoluble fractions, in which the amount of the latter increased when the VBDC units in the copolymer photoiniferter used increased. In the presence of UV light, VBDC polymerized without a radical initiator, leading to benzene-soluble and -insoluble polymers as a result of participation of the styryl double bond in the polymers produced. However, the photopolymerization of St with a catalytic amount of VBDC as a photoiniferter gave a benzene-soluble polymer that contains a styryl double bond and a *N,N*-diethyldithiocarbamyl group at the polymer chain ends, i.e., a macromer–iniferter.

Introduction

In previous papers,[1-6] monomeric and polymeric compounds with *N,N*-diethyldithiocarbamyl groups have been reported to serve as a photoiniferter of living radical polymerization in homogeneous systems. Therefore, the use of these iniferters (initiator–transfer agent–terminator) has been found to be effective for the synthesis and design of various functional and block polymers.[4-6]

If such iniferters having a polymerizable double bond, i.e., monomer–iniferter, are synthesized and used successively as both monomer and iniferter macromers and graft copolymers would be obtained according to Scheme I, where B is a *N,N*-diethyldithiocarbamyl ($-SC(S)NEt_2$) group.

Since St is a highly polymerizable monomer and benzyl *N,N*-diethyldithiocarbamate is an effective photoiniferter,[6] 4-vinylbenzyl *N,N*-diethyldithiocarbamate (VBDC) is also expected to serve as a monomer–iniferter. From these viewpoints, VBDC was prepared and its reactivities as both monomer and iniferter were evaluated. Moreover, the

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