Macromolecules **1985**, *18*, 835–840

(8) Shoun, R. R.; McDowell, W. J. "Actinide Extractants: Development, Comparison, and Future"; Navratil, J. D., Schulz, W. W., Eds.; American Chemical Society: Washington, DC, 1980; ACS Symp. Ser. No. 117, Chapter 6.
(9) (a) Marhol, M. *At. Energy Rev.* **1966**, 63. (b) Vernon, F.; Nyo, K. M. *Sep. Sci. Technol.* **1978**, *13*, 263. (c) Small, H. *J. Inorg. Nucl. Chem.* **1961**, *18*, 232.
(10) An initial report has appeared: Alexandratos, S. D.; McDowell, W. J. *Sep. Sci. Technol.* **1983**, *18*, 1715.
(11) Pal, G. C.; Chakravarti, A. K.; Sengupta, M. *Ion Exch. Membr.* **1974**, *2*, 21.
(12) Abrams, I. M. U.S. Patent 2 844 546, 1958.
(13) Small, H. *Ind. Eng. Chem. Prod. Res. Dev.* **1967**, *6*, 147.
(14) Fleming, C. A.; Nicol, M. J. *J. S. Afr. Inst. Min. Metall.* **1980**, *80*, 89.
(15) Kennedy, J. *Chem. Ind. (London)* **1956**, 137.
(16) Kobayashi, S.; Suzuki, M.; Saegusa, T. *Macromolecules* **1983**, *16*, 1010.
(17) Vernon, F.; Nyo, K. M. *Anal. Chim. Acta* **1977**, *93*, 203.
(18) Guilbault, L. J.; Murano, M.; Harwood, H. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1065.
(19) Nishide, H.; Oki, N.; Tsuchida, E. *Eur. Polym. J.* **1982**, *18*, 799.
(20) Smid, J.; Shah, S. C.; Varma, A. J.; Wong, L. *J. Polym. Sci., Polym. Symp.* **1978**, *64*, 267.
(21) Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962; Chapter 5.
(22) Barrett, J. H. U.S. Patent 3 843 566, 1974.
(23) Kun, K. A.; Kunin, R. *J. Polym. Sci., Part A-1* **1968**, *6*, 2689.
(24) McMaster, E. L.; Glesner, W. K. U.S. Patent 2 764 563, 1956.
(25) Bogoczek, R.; Surowiec, J. *J. Appl. Polym. Sci.* **1981**, *26*, 4161.
(26) Marhol, M.; Beranova, H.; Cheng, K. L. *J. Radioanal. Chem.* **1974**, *21*, 177.
(27) Kressman, T. R. E.; Tye, F. L. British Patent 726 918, 1955.
(28) Drake, L. R. U.S. Patent 2 764 562, 1956.
(29) Hisayama, H.; Utsonomiya, Y. Japanese Patent 14 496, 1962.
(30) In this equation and in all other representations of secondary sites, adjacent units are used only for convenience in drawing; indeed, a large number of the secondary sites must involve interchain cross-linking as the linear polystyrene experiments show (Table V).
(31) Brown, M. P.; Silver, H. B. *Chem. Ind. (London)* **1961**, 24.
(32) Kosolapoff, G. M.; Huber, W. F. *J. Am. Chem. Soc.* **1947**, *69*, 2020.
(33) Frank, A. W. *J. Org. Chem.* **1959**, *24*, 966.
(34) Ford, W. T.; Lee, J.; Tomoi, M. *Macromolecules* **1982**, *15*, 1246.
(35) Bregman, J. I.; Murata, Y. *J. Am. Chem. Soc.* **1952**, *74*, 1867.
(36) (a) Greig, J. A.; Sherrington, D. C. *Eur. Polym. J.* **1979**, *15*, 867. (b) Farrall, M. J.; Frêchet, J. M. J. *J. Am. Chem. Soc.* **1978**, *100*, 7998.
(37) Pepper, K. W.; Paisely, H. M.; Young, M. A. *J. Chem. Soc.* **1953**, 4097.
(38) Alexandratos, S. D.; Wilson, D. L.; Strand, M. A.; Quillen, D. R.; Walder, A. J.; McDowell, W. J. *Macromolecules*, following paper in this issue.
(39) Arcus, C. L.; Matthews, R. J. S. *J. Chem. Soc.* **1956**, Part IV, 4207.
(40) Blake, C. A.; Brown, K. B.; Coleman, C. F. Report 1964; Oak Ridge National Laboratory: Oak Ridge, TN, 1955.

Metal Ion Extraction Capability of Phosphinic Acid Resins: Comparative Study of Phosphinic, Sulfonic, and Carboxylic Resins Using Zinc Ions

Spiro D. Alexandratos,* David L. Wilson, Marc A. Strand, Donna R. Quillen, and Anthony J. Walder

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

W. J. McDowell

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.
Received July 18, 1984

ABSTRACT: Bifunctional cation-exchange resins were evaluated as zinc ion extractants. Bifunctionality consisted of either primary and secondary phosphinic acid ligands or primary phosphinic acid/secondary phosphine oxide ligands. The performance of these phosphinic resins was compared to the zinc extraction ability of comparably cross-linked polystyrene-based sulfonic and carboxylic resins. For the phosphinic resins, the degree of extraction is determined by the initial ratio (R_i) of zinc ions to be absorbed and acid sites to carry out the exchange; the equilibrium point is independent of matrix rigidity to 15% divinylbenzene (DVB). Further, there is no dependence of zinc extraction ability on the total capacity or the presence of primary/secondary vs. primary only phosphinic acid groups vs. primary acid/secondary phosphine oxide groups at any given R_i level. For sulfonic resins, on the other hand, the zinc loading on the resin decreases at a given R_i as the amount of DVB increases from 2% to 15%. A similar conclusion is valid for the carboxylic resins although the zinc extraction is lower under similar conditions. In general, the phosphinic resins display superior extraction ability under comparable conditions. The unique dependence on R_i alone displayed by the phosphinic ligands is explained on the basis of ion pair formation. Current studies show that *phosphinic acid resins operate by both an ion-exchange and redox mechanism* depending on the reduction potential of the metal.

Introduction

The application of commercial ion-exchange resins to metal ion recovery from aqueous solutions is a concept which has received extensive study.[1] Strong acid cation exchangers are produced by covalent bonding of sulfonic acid groups usually to a cross-linked polystyrene network.[2] Contact with an aqueous solution of a metal ion allows for cation exchange to occur and the metal can then be recovered from the polymer by elution with an aqueous mineral acid solution. The ion-exchange effectiveness of a strong acid resin can be offset by a lack of selectivity, especially when the metal ion of interest is in trace amounts relative to common metals such as the alkali metal ions.[3] Selectivity is enhanced with the weak acid cation-exchange resins wherein carboxylate groups are bonded to either a styrenic or ethylenic network,[4] but this leads to a decreased ability to exchange in the acidic pH region (which is usually the region of interest in waste metal recovery).[5] Novel ion-exchange resins have been synthesized by bonding selective ligands onto commercial supports for the purpose of recovering specific metals;[6] such resins illustrate important principles, but are usually not commercially feasible due to their cost.

In liquid–liquid extractions, a cation-containing aqueous phase at a given pH is contacted with an extractant-containing organic phase; the organic phase consists of an

0024-9297/85/2218-0835$01.50/0

acidic or basic extractant (such as a sulfonic acid, a phosphoric acid, or an amine) and/or a neutral extractant (such as tributyl phosphate) usually in a solvent (toluene, hexane, etc.). Contact of the two phases leads to an extraction of the metal ion from the aqueous into the organic phase by an ion-exchange or ionic-coordination mechanism. The principal difference in solid–liquid extractions is that the extractant ligand is immobilized on a polymer network in bead form; the polymer then binds the metal ion as the aqueous phase flows through the column.

Liquid–liquid extractions have a number of advantages: they are well-characterized systems with a large number of extractants being available; metal ion uptake can be rapid; and the system can be easily adjusted to the demands of the aqueous stream by varying the extractant feed. The system's disadvantages include extractant loss due to solubility into the aqueous phase as well as extractant loss by entrainment during phase separation, and the additional aqueous pollution from solubility/entrainment of the organic solvent if used due to extractant viscosity or physical state. Solid–liquid extractions also encompass disadvantages: they have a higher initial cost due to the polymer synthesis, they can exhibit lower rates of extraction than liquid extractants due to diffusional limitations, and there can be extractant loss through polymer attrition (mechanical limitation). Polymeric systems, though, enjoy some very important advantages: extractant loss through solubility and entrainment is clearly eliminated; the polymer support is the diluent and so no additional solvent is required; and the system is readily adaptable to the long-term continuous operation most appropriate to metal ion recovery from dilute solutions.

Our research to date has involved the synthesis of polymer-supported extractants which are designed (1) to display greater selectivity than the sulfonic ligands, (2) to exchange at a much lower pH than the carboxylic ligands, and (3) to be practical for large-scale applications. With these considerations in mind, the principal focus of our investigation has been on the synthesis of polystyrene networks to which phosphinic acid groups are covalently bonded as ion-exchange ligands. Polystyrene provides an ideal substrate in that it is a commercial commodity, it is chemically resistant to degradation under field conditions, a wide variety of ligands can be bonded to it via aromatic substitution reactions, and it can be synthesized at any level of matrix rigidity (to improve attrition resistance) or macroporosity (to improve exchange kinetics). Phosphorus acids possess intermediate acidity[7] and should thus display greater selectivity than the sulfonic groups while showing more effective exchange than the carboxylic ligands in acidic solutions. In fact, polymeric phosphonic acids are known to be more selective than the sulfonic acids while providing ion-exchange capability at significantly lower pH values than the carboxylic acids.[8] This advantage should be maintained with phosphinic acids attached to a polystyrene support. The experimental procedure that we have proposed has allowed for an additional, perhaps more important, advantage: the synthesis of a phosphinic acid/phosphine oxide bifunctional polymeric extractant.[9,10] Studies of liquid–liquid extraction systems have shown that the addition of both an ionic and neutral extractant within the same organic phase can, in some cases, allow for a synergistic extraction of the metal ion in which the distribution to the organic phase is more effective than would be expected from the sum of the separate extractants used alone.[11] To date, synergistic extraction has been observed in liquid–liquid extraction studies, but has not been demonstrated in exchange studies with resins. By combining both groups on one polymer, we have the first example of a system that can display cation-exchange synergism in solid–liquid systems. By synthesizing the polystyrene support under a number of conditions, we can control the variables which maximize attrition resistance and exchange kinetics; by functionalizing the polystyrene so that ion-exchange and neutral-coordinating ligands are in proximity, we hope to maximize the effectiveness of metal ion extraction at a high level of selectivity.

Our initial studies on the application of the phosphinic acid/phosphine oxide resins for metal ion extractions are detailed in this report. In order to provide a basis for comparison with other ligands, we have synthesized sulfonic acids and carboxylic acids on polystyrene supports which are identical with those used with our phosphorus ligands. Though it is often not the case, metal ion analyses should be compared among different ligands only if precautions are taken to ensure identical supports since even differences in cross-link level can lead to differences in extent of extraction and observed selectivities.[12] This study also provides a comparative study of phosphorus, sulfur, and carbon acids and attempts to isolate the effect of the ligand by holding the polymer support constant.

Results and Discussion

Synthesis of the Polystyrene Support. The polystyrene support was synthesized in bead form (1-mm diameter) by suspension polymerization[13] and has been detailed earlier.[10] Both gel and macroporous (or macroreticular (MR))[14] resins have been investigated. Introduction of macroporosity is important not only from a kinetic standpoint but also because MR beads are much more resistant to organic and inorganic fouling than beads without macropores (i.e., gel beads); this decreases the importance of pretreating the water to remove foulants (humic acid, colloidal oxides, etc.) prior to metal ion extraction.[15]

Functionalization to Phosphorus Resins. Synthesis of the phosphorus resins has been reported in detail.[10] The polystyrene support (2–15 wt % DVB) was functionalized with PCl_3 and various levels of $AlCl_3$ catalyst at given temperatures (−78 to +73 °C). Final resin capacity was found to be dependent on the catalyst level and temperature. Functionalized beads which were hydrolyzed in 1 N NaOH yielded resin with secondary and/or primary phosphinic acid groups while beads hydrolyzed in water yielded resin with primary acid and secondary phosphine oxide groups. The resin was conditioned to the acid form and analyzed by NaOH titration to give total acidity, the percent elemental phosphorus determined to give total substitution by phosphorus moieties, and an iodine oxidation to quantify the presence of primary phosphinic acid. The resins used in the current study are summarized in Table I and the synthesis summarized in Figure 1.

Functionalization to Sulfonic Acid Resins.[2] Polystyrene gel beads cross-linked with 2%, 10%, and 15% DVB were swollen in 1,2-dichloroethane and then reacted with concentrated H_2SO_4 at 130 °C over a 3-h period (Figure 1). The resins were analyzed by NaOH titration to give total acidity (Table I).

Functionalization to Carboxylic Acid Resins. In order to maintain support comparability with the sulfonic and phosphinic resins, we synthesized a polystyrene-supported carboxylic acid resin rather than use the conventional acrylic resins. Synthesis was found to proceed most efficiently by oxidizing the chloromethylene group on a styrenic network. Poly(vinylbenzyl chloride) gel beads cross-linked with 2%, 10%, and 15% DVB were synthesized from vinylbenzyl chloride monomer following the

Table I
Acid Capacities of Phosphinic, Sulfonic, and Carboxylic Resins

resin	DVB, %	type	functionalizn	capacity, mequiv/(g of dry resin)				
				acid		total OH	total %P[a]	theory[b]
				primary	secondary			
			Phosphinic Resins					
DR49A	2	gel	0.77 mol of $AlCl_3$/73 °C	2.34	2.05	4.39	4.85	4.46
DR49B	10	gel	0.77 mol of $AlCl_3$/73 °C	1.94	1.32	3.26	3.77	4.09
DR49C	15	gel	0.77 mol of $AlCl_3$/73 °C	1.13	c	1.39	2.45	3.87
DR08B	2	MR	0.77 mol of $AlCl_3$/0 °C	1.45	0	1.22[d]	1.30	
DR08C	2	MR	0.77 mol of $AlCl_3$/23 °C	2.08	0	2.01[e]	2.69	
DR08D	2	MR	0.77 mol of $AlCl_3$/73 °C	2.31	2.28	4.75	4.59	
MS14A	2	MR	0.77 mol of $AlCl_3$/73 °C	2.31	2.10	4.41	4.61	
AW06A	2	MR	0.20 mol of $AlCl_3$/73 °C	2.43	0	2.02	2.39	
AW06D	2	MR	1.2 mol of $AlCl_3$/73 °C	2.26	2.69	4.95	5.17	
AW12D	2	MR	1.2 mol of $AlCl_3$/23 °C	2.28	0	2.06[e]	3.01	
AW61B	linear		0.77 mol of $AlCl_3$/73 °C			4.52	4.95	
AW61C	2	gel	0.77 mol of $AlCl_3$/73 °C	2.40	2.23[f]	2.40	4.83	
			Sulfonic Resins					
DW31D	2	gel	concd H_2SO_4/130 °C			5.00		5.29
DW31A	10	gel	concd H_2SO_4/130 °C			4.76		4.80
DW31B	15	gel	concd H_2SO_4/130 °C			3.16		4.46
			Carboxylic Resins					
DW91A	2	gel	KOH/80 °C; HNO_3/30 °C			6.55		6.43
DW91C	10	gel	KOH/80 °C; HNO_3/30 °C			5.51		5.44
DW91D	15	gel	KOH/80 °C; HNO_3/30 °C			5.33		4.83

[a] Capacity based on %P elemental analysis. [b] Theoretical capacity assuming 100% reaction and inertness of divinylbenzene/ethylvinylbenzene. [c] Difference in total OH vs. total %P due to OH^- reagent inaccessibility at higher cross-link level; powdering resin gives total OH = total %P; secondary acid then calculates to 1.32 mequiv/g. [d] Obtained by powdering resin due to reagent inaccessibility. [e] Obtained on whole and powdered beads; difference with total %P due to inert tertiary phosphine oxide (ref 10). [f] Phosphine oxide; resin obtained via neutral hydrolysis.

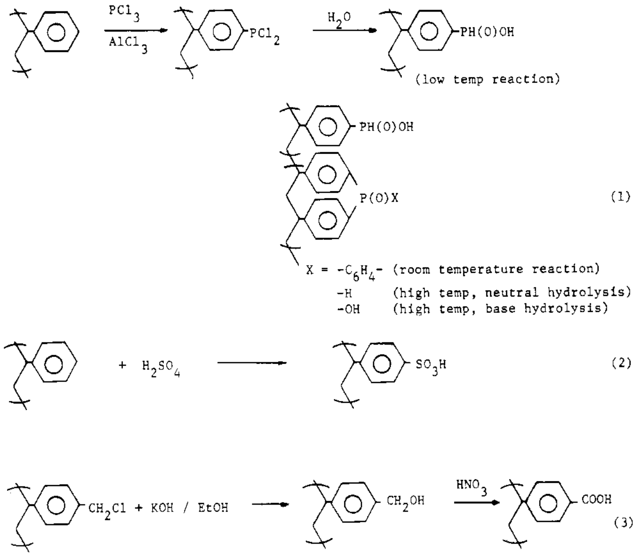

Figure 1. Synthesis of polystyrene-supported phosphinic (1), sulfonic (2), and carboxylic (3) acid extractants.

same experimental procedure as with polystyrene. The chloromethylene groups were first hydrolyzed to hydroxymethylene groups by refluxing with alcoholic KOH for 24 h and then further oxidized to carboxylic groups by heating at 30 °C for 24 h with concentrated HNO_3 (Figure 1). NaOH titration provided the determination of total acidity (Table I). Complete conversion to the alcohol prior to oxidation is crucial to avoiding nitration of the resin by HNO_3 as studies with liquid-phase analogues showed.[16]

Zinc Analysis. General Procedure. The zinc-exchange capacity of each resin given in Table I was determined at various levels of initial zinc solution concentration per milliequivalent of exchangeable acid resin capacity. Since only protons accessible to the metal ion should be considered, the total acidity based on the NaOH titration is used in all calculations given that this technique is also subject to reagent accessibility limitations. The extraction equilibrium studies were set up at different initial ratios (R_i values) of milliequivalents of zinc ions to resin protons; R_i values of 0.02–1.50 were most commonly utilized.

Five-milliliter samples of 4 N $NaNO_3$ solution containing varying concentrations of zinc (as the nitrate) were contacted with 1 mequiv of acid resin which provided a constant ionic strength throughout the exchange. The samples were equilibrated for a 17-h period and the ion exchange was determined by the loss from solution of radiotracer zinc. Measuring the final pH of the solution (found to range between 0.6 and 1.0) gave a qualitative indication of the number of protons exchanged.

Gel Phosphinic Resins. The zinc extraction ability of the gel phosphinic resins (DR49A–C) is indicated in Table II, which reports the extent of ion exchange, i.e., the milliequivalents of zinc on the resin relative to the maximum number of sites available (%Zn loading), and the amount of zinc absorbed from solution, as a function of the initial ratio of zinc to acid sites (R_i). The results indicate that the gel phosphinic resins are identical in their degree of loading and zinc absorption up to 15% DVB cross-linking under equilibrium conditions at any given R_i value. This is emphasized by placing all of the %Zn loading vs. R_i results on a single graph (v.i.).

Macroporous Phosphinic Resins. Since the macroporous resins as used were not completely dry but contained a finite amount of water in the pores, the addition of a given weight of MR resin to a zinc solution effectively dilutes the solution. The volume of water in the macropores is calculated by the difference in water content of an MR and a comparably cross-linked gel at the same functionality level and dry weight (assuming a density for water of 1.0 g/mL); from this, the dilution of metal ion which occurs by water in the macropores is calculated and is that which we have termed the macroporosity dilution factor (MDF). The manner in which this factor is calcu-

Table II
Zinc Analyses of Phosphinic Acid Resins at Indicated Cross-Link Levels and Acid Capacities[a]

Gel Resins at Different Cross-Link Levels

	DR49A (2%; 4.39 mequiv)				DR49B (10%; 3.26 mequiv)				DR49C (15%; 1.39 mequiv)			
R_i	0.028	0.36	0.66	1.00	0.027	0.39	0.71	1.06	0.10	0.41	1.00	1.50
Zn loading, %	2.06	17.8	24.1	32.0	1.80	18.7	27.1	35.0	6.20	16.9	29.8	44.2
Zn absd from soln, %	74.0	48.7	36.6	32.4	65.9	47.4	38.2	33.1	61.6	40.9	29.6	29.3

MR Resin with MDF Included

	MS14A (2%; 4.41 mequiv)									
R_i	0.024	0.048	0.096	0.19	0.38	0.48	0.57	0.67	0.77	0.86
Zn loading, %	1.55	2.99	5.54	9.70	16.5	18.8	21.7	24.4	25.0	26.6
Zn absd from soln, %	65.6	61.4	57.1	50.6	42.6	39.7	37.8	36.5	32.8	30.7

2% DVB MR Resins at Different Functionality Levels

	DR8B (0.84 mequiv)			DR8C (2.01 mequiv)			DR8D (4.59 mequiv)		
R_i	0.24	2.4	3.6	0.10	1.0	1.5	0.04	0.4	0.65
Zn loading, %	8.95	39.3	45.7	6.01	31.9	40.5	2.95	19.7	21.7
Zn absd from soln, %	38.4	16.6	12.8	60.6	32.1	27.2	66.6	45.3	33.4

	AW06A (2.02 mequiv)			AW06D (4.95 mequiv)			AW12D (2.09 mequiv)		
R_i	0.10	0.99	1.48	0.041	0.41	0.61	0.11	1.12	1.68
Zn loading, %	4.84	24.9	32.1	2.68	17.5	22.6	6.09	36.8	46.2
Zn absd from soln, %	48.5	25.1	21.6	65.7	43.0	37.3	55.7	32.9	27.5

[a] Per gram.

lated is as follows wherein concentration ratios are replaced by counts per minute (cpm) ratios of the radiotracer ^{65}Zn.

$$\text{mL(H}_2\text{O) in macropores} = (1 - (\text{\% solids in MR})/(\text{\% solids in gel}))(\text{wt MR resin})$$

$$(\text{Zn}^{2+})_b \propto \text{cpm}_b$$

$$(\text{Zn}^{2+})_a \propto \text{cpm}_a = \text{cpm}_b(b/a)$$

where b = volume of aqueous solution only (and corresponding zinc concentration in the absence of resin), a = volume of aqueous solution and macropores (and corresponding calculated zinc concentration), and

$$\text{MDF} = \text{cpm}_a/\text{cpm}_b \equiv b/a$$

Any further decrease in metal ion concentration from the aqueous phase must then result from ion exchange:

$$(\text{Zn}^{2+})_f^{\text{beads}} \text{ by ion exchange} = \left(\frac{\text{cpm(beads)}}{\text{cpm}_a}\right) \times (\text{Zn}^{2+})_i^{\text{soln}} = \left(1 - \frac{\text{cpm(soln)}_f}{\text{MDF(cpm}_b)}\right)(\text{Zn}^{2+})_i^{\text{soln}}$$

It is interesting to note that in a complete study of a fully functionalized MR resin (MS14A, Table II), no significant difference in extractability for the MR vs. the gel resins is found once this factor is introduced.

A more complete study with 2% DVB MR resins at different functionality levels is also given in Table II (DR8B–D). The MDF for DR8B was approximated due to difficulties in synthesizing a low functionality gel resin. A comparison of DR8C,D with DR49A–C shows good agreement in %Zn loading as a function of R_i. DR8D and MS14A are different resins synthesized under the same conditions; a comparison of the zinc values shows the precision to be quite good. Generally speaking, the amount of zinc absorbed from an aqueous solution containing a given amount of zinc is dependent only on the number of acid sites and not on the capacity of the resin or on the presence of bifunctionality (v.i.). Comparison of results from AW06A,D (resins made at different catalyst levels at high temperature) with resin AW12D (high catalyst level at low temperature) indicates the latter to be somewhat superior in zinc extraction ability; a repeat synthesis yielded identical results and the concept is currently under study.

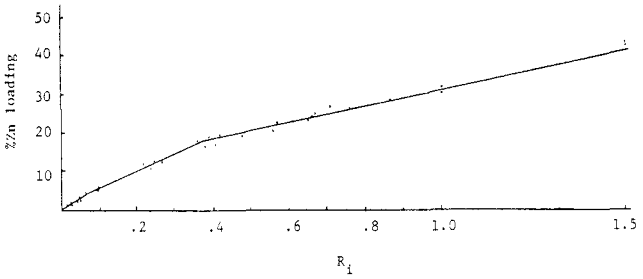

Figure 2. %Zn loading vs. R_i for the phosphinic resins.

General Conclusions on Phosphinic Resins. All phosphinic resins, synthesized under a wide variety of conditions and listed in Table I, act in a comparable manner. This is best indicated by plotting Zn loading as a function of R_i. Figure 2 indicates the shape of the curve for the phosphinic ligands; the plot derives from all the phosphinic resins; loading values are found to be within 2%, with R_i values ≥1 showing scatter up to ±4%. The important conclusion is that for phosphinic resins, R_i is the controlling variable: the degree of extraction is determined by the ratio of zinc ions to be absorbed and the acid sites to carry out the exchange. The equilibrium point is independent of matrix rigidity to 15% DVB and macroporosity. The conditions under which macroporous resins will display superior kinetic properties is currently under study.

Note that the phosphinic acid correlation also includes zinc results from fully functionalized linear polystyrene

Table III
Zinc Analyses of Phosphinic Acid Resins with Acid Exchange Values

	DR49A (primary/secondary acid)				AW61B (primary/secondary acid)			AW61C (primary/secondary oxide)		
R_i	0.028	0.36	0.66	1.00	0.055	0.55	0.83	0.38	0.32	0.56
Zn^{2+} absd, mequiv/g	0.09	0.78	1.06	1.41	0.160	1.14	1.52	0.061	0.34	0.50
H^+ exchanged, mequiv/g	1.54	2.12	2.98	3.06	1.84	2.78	3.24	0.30	0.35	0.45
Zn loading, %	2.06	17.8	24.1	32.0	3.53	25.3	35.0	2.55	14.1	21.1
Zn absd from soln, %	74.0	48.7	36.6	32.4	64.6	45.9	42.3	66.4	43.9	37.5

Table IV
Comparative Study with Sulfonic and Carboxylic Gel Resins

Sulfonic Resins

	DW31D (2%; 5.00 mequiv)			DW31A (10%; 4.76 mequiv)			DW31B (15%; 3.16 mequiv)		
R_i	0.1	1.0	1.5	0.1	1.0	1.5	0.1	1.0	1.5
Zn loading, %	4.31	41.0	58.2	2.44	24.3	30.2	2.00	17.5	22.1
Zn absd from soln, %	43.2	41.1	38.9	23.8	23.7	19.6	20.1	17.8	15.0

Carboxylic Resins

	DW91A (2%; 6.55 mequiv)			DW91C (10%; 5.51 mequiv)			DW91D (15%; 5.33 mequiv)		
R_i	0.1	1.0	1.5	0.1	1.0	1.5	0.1	1.0	1.5
Zn loading, %	2.81	27.6	40.0	1.32	15.6	19.8	0.97	7.34	10.7
Zn absd from soln, %	28.3	27.6	26.6	13.1	15.6	13.2	9.74	7.34	7.13

(0% DVB; AW61B) and the bifunctional phosphinic acid/secondary phosphine oxide resin (2% DVB gel resin; AW61C). The pH measurements can be used to approximate the number of protons released into solution via ion exchange. As shown in Table III, the pH measurements strongly support the acid/oxide bifunctionality hypothesis: for all phosphinic resins except AW61C, the number of protons released into solution exceeds the milliequivalents of zinc exchanged; this is due to further exchange with sodium ions. AW61C is the only resin where the number of protons released equals the milliequivalents of zinc ions exchanged for all but the most dilute solutions, suggesting a superior selectivity for zinc over sodium for this resin. Current studies are emphasizing this resin type with a wide variety of metals.

Sulfonic Resins. In contrast to the phosphinic resins, gel sulfonic resins (DW31D,A,B) show a dependency on the cross-link level when measuring the Zn loading at a given R_i value (Table IV). For sulfonic ligands, Zn loading decreases at a given R_i as the percent of DVB increases, making %DVB the controlling variable; e.g., at an R_i of 1.0, the Zn loading = 41% (for 2% DVB resin), 24% (for 10% DVB resin), and 18% (for 15% DVB resin). In each case, the number of protons released greatly exceeds the milliequivalents of zinc ions exchanged (as indicated by pH measurements) showing the importance of exchange with sodium ions.

Carboxylic Resins. The gel carboxylic resins (DW91A,C,D) were studied under the same low pH conditions that the phosphinic and sulfonic resins were studied. With the carboxylic resins, the Zn loading is inversely proportional to the cross-link level, as it is with the sulfonic resins, but at a lower level (Table IV): at an R_i of 1.0, the Zn loading = 28% (for 2% DVB resin), 16% (for 10% DVB resin), and 7% (for 15% DVB resin). Final pH values show that the number of protons released is much less than the milliequivalents of zinc ions absorbed, suggesting that the carboxylic resins operate by a neutral coordination mechanism at low pH (pH ≤ 2) and not by an ion-exchange mechanism.

Conclusions

The superiority of the phosphinic resins over the sulfonic and carboxylic resins for zinc ion recovery, at the commercially useful level of 10% DVB cross-linking, can be seen by comparing Figure 2 with Table IV. Under comparable initial conditions, the phosphinic resins load to a greater extent than either the sulfonic or carboxylic resins where the Zn^{2+} directly competes with a large excess of alkali metal ion. Assuming that sodium ions are representative of common impurities that one does not want to extract, the selectivity displayed by the phosphinic acid relative to the sulfonic acid for zinc over sodium ions is a significant observation.

The unique dependence on R_i alone displayed by the phosphinic acid groups may be explained on the basis of ion pair formation. The phosphinic acids are intermediate acids which require contact ion pair formation for anionic stabilization upon metal ion complexation. Zinc's divalency and greater polarizability than sodium allows for the necessary contact ion pair formation. Matrix rigidity is overcome for covalent stabilization to occur making R_i the controlling variable.

The sulfonic acids, on the other hand, are strong acids and the sulfonate anion is relatively stable; loose ion pair formation can occur due to the anionic stability. Since no added stabilization is obtained through contact ion pair formation, increased matrix rigidity decreases the selectivity for the divalent zinc over the univalent sodium making %DVB the controlling variable.

The neutral coordination displayed by the carboxylic ligands is much more similar to the loose ion pair of the sulfonic groups than the contact ion pair of the phosphinic groups making %DVB, once more, the dominant variable.

Consistent with the results and the concept of ion pair formation is the fact that zinc is much more likely to bond by coordination than is sodium[17] and the phosphinic oxygens are much stronger electron donors than are the oxygens on sulfur or carbon.[18] The strength of the metal–ligand interaction is balanced by the matrix rigidity and determines the zinc/sodium selectivity.

Current Studies. Phosphinic Resins as Redox Polymers

The P–H bond in the phosphinic resin is oxidizable as indicated by titration with potassium triiodide. We have recently found that it acts as a reducing agent in the presence of metals having an appropriate reduction potential allowing for the isolation of zerovalent metal. Metal ion extraction studies with mercuric nitrate in place of zinc nitrate have been done with the phosphinic resins DR49A, DR49C, and MS14A. Our complete results will be reported shortly; the following observations are most important:

(1) At an $R_i = 0.1$, the phosphinic resins absorb 90–95% of the Hg^{2+} in solution; at an $R_i = 1.0$, the resins absorb 70% of the mercuric ions as measured by radiotracer mercury.

(2) Under identical conditions ($R_i = 1.0$), the sulfonic resin (DW31A) absorbs 25% and 15%, respectively, of the mercuric ions.

(3) The phosphinic resins all undergo a color change from white to metallic gray while the liquid phase remains clear and colorless. The resins remain white in all studies with zinc.

(4) An identical effect is predicted for Ag^+ ions given that silver and mercury have similar reduction potentials; while not quantified, the same color change is seen on the resin. We predict an even stronger affinity for gold given its greater reduction potential.

(5) NaOH titration curves show the resins to be oxidized after contact with the Hg^{2+} solution given the presence of phosphonic acid groups; no such oxidation occurs upon 17-h contact with 4 N HNO_3 at room temperature.

The ability of *phosphinic acid resins to function by both ion-exchange and redox mechanisms* is under active study in our laboratory.

Experimental Section

All reagents were purchased commercially and used without further purification unless otherwise noted. The accompanying paper details the copolymer synthesis, the functionalization to the phosphorus acid resin, and the methods of characterization.[10]

Polymer-Supported Sulfonic Resin. Copolymer beads (10 g) are placed with 20.6 g of ethylene dichloride, 88.4 g of 96% H_2SO_4, and 1.79 g of H_2O into a 250-mL round-bottom flask equipped with an overhead stirrer, condenser, and thermometer. The system is stirred at room temperature for 15 min, then heated to 130 °C over a 3-h period, held at 130 °C for 15 min, and slowly quenched with water. The resin is washed with water and conditioned with 1 L of H_2O, 1 N NaOH, H_2O, 1 N HCl, and H_2O, each with 1-h elution times.

Polymer-Supported Carboxylic Resin. Vinylbenzyl chloride (VBC)/DVB copolymer beads are synthesized as detailed for styrene/DVB. VBC copolymer beads (10 g) are swollen in toluene, added to 400 mL of alcoholic KOH (25 wt %) in a 500-mL round-bottom flask and refluxed for 24 h. The beads are then separated, washed 4 times with EtOH, and eluted with water until no longer basic. The beads are suction-dried and placed in a 500-mL round-bottom flask with 400 mL of concentrated HNO_3 and kept at 30 °C for 24 h. The beads are washed sequentially with 250 mL of 10, 5, 1, and 0.1 M HNO_3. The resin is then washed with water and conditioned as above.

Zinc Analysis. Each series of vials for a given resin contained a given zinc concentration in 5 mL of solution and a quantity of resin containing 1 mequiv of acid sites (usually about 0.5 g). An amount of zinc stock solution (2 N $Zn(NO_3)_2$ in 2 N $NaNO_3$) was used to yield initial milliequivalent ratios (R_i) of zinc ions to resin protons in the region 0.02–1.5; the remainder of the 5-mL solution consisted of 4 N $NaNO_3$. Each 5-mL solution contained 0.025 μCi of ^{65}Zn initially and the solutions were counted after a 17-h equilibration period. Counting was done in a NaI–TlI well-type scintillation counter. A multichannel analyzer with a region-integrating feature allowed only the 1.1-MeV ^{65}Zn peak to be counted, thus reducing background count rate and increasing counting accuracy. One-milliliter samples were counted twice, each for 1 min, and the cpm's averaged for all calculations. The solution pH was measured with a Brinkmann pH meter.

Acknowledgment. We gratefully acknowledge the financial support of the Department of Energy through the Office of Basic Energy Sciences (DE-AS05-83ER13113). We also acknowledge the expert technical assistance of Mr. Gerry N. Case (ORNL).

References and Notes

(1) (a) Marhol, M. *At. Energy Rev.* **1966**, *4*, 63. (b) Marhol, M. "Ion Exchangers in Analytical Chemistry"; Svehla, G., Ed.; Elsevier: Amsterdam, 1982; Compr. Anal. Chem. Vol. 14. (c) Myasoedova, G. V.; Savvin, S. B. *Zh. Anal. Khim.* **1982**, *37*, 499. (d) Bogoczek, R.; Surowiec, J. *J. Appl. Polym. Sci.* **1981**, *26*, 4161.

(2) Bortnick, N. M. U.S. Patent 3 037 052, 1962.

(3) Diamond, R. M.; Whitney, D. C. In "Ion Exchange"; Marinsky, J. A., Ed.; Marcel Dekker: New York, 1966; Vol. 1, Chapter 8.

(4) Brajter, K.; Miazek, I. *Talanta* **1981**, *28*, 759.

(5) Dorfner, K. "Ion Exchangers"; Ann Arbor Science: Ann Arbor, MI, 1972; Chapter 4.

(6) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557.

(7) (a) Soldatov, V. S.; Manenok, G. S. *Russ. J. Phys. Chem.* (*Engle Transl.*) **1967**, *41*, 1192. (b) Soldatov, V. S.; Novitskaya, L. V. *Ibid.* **1965**, *39*, 1453.

(8) Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962; Chapter 5.

(9) Alexandratos, S. D.; McDowell, W. J. *Sep. Sci. Technol.* **1983**, *18*, 1715.

(10) Alexandratos, S. D.; Strand, M. A.; Quillen, D. R.; Walder, A. J. *Macromolecules*, preceding paper in this issue.

(11) Shoun, R. R.; McDowell, W. J. "Actinide Extractants: Development, Comparison, and Future"; Navratil, J. D., Schulz, W. W.; Eds.; American Chemical Society: Washington, DC, 1980; ACS Symp. Ser. No. 117, Chapter 6.

(12) Green, B. R.; Hancock, R. D. *Hydrometallurgy* **1981**, *6*, 353.

(13) Barrett, J. H.; U.S. Patent 3 843 566, 1974.

(14) Kun, K. A.; Kunin, R. *J. Polym. Sci., Part A-1* **1968**, *6*, 2689.

(15) Semmens, M. J. *AIChE Symp. Ser.* **1975**, *71*, 214.

(16) Alexandratos, S. D.; Walder, A. J. *J. Org. Chem.*, to be submitted.

(17) Sekine, T.; Hasegawa, Y. "Solvent Extraction Chemistry"; Marcel Dekker: New York, 1977; Chapter 2.

(18) Reference 17, Chapter 7.