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SYNTHESIS OF NOVEL CHELATING RESINS CONTAINING DITHIOPHOSPHORIC FUNCTIONALITY AND COMPARISON TO ANALOGOUS SOLVENT IMPREGNATED RESINS

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ABSTRACT

Functional polymers (**III**–**VIII**) incorporating thiophosphoric acids were synthesized. Analogous solvent impregnated resins (SIRs) were made from polyvinyl pyridine and polyvinyl benzyl ammonium types of ionic polymers by impregnation of di-(2-ethylhexyl)-dithiophosphoric acid. The polymers and their metal complexes were characterized by FTIR. Surface area measurements of the SIR-type polymer reveal surface area and pore volume reduction upon metal ion complexation. Both covalent and impregnated-type polymers show selectivity towards Cu, Cd,

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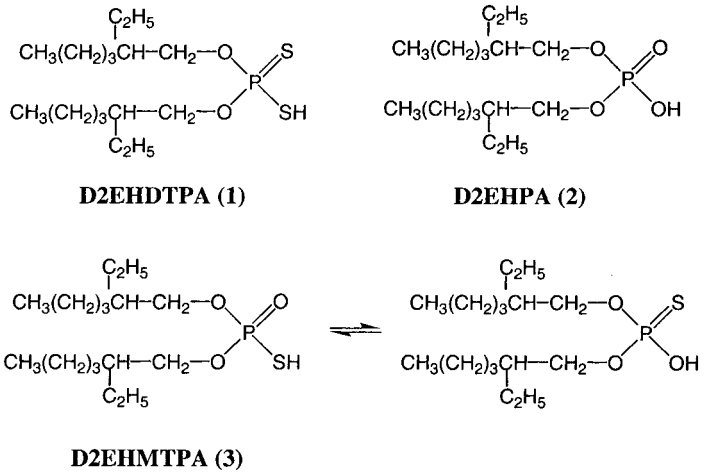
Ni, and Pb. Solvent impregnated resins are more effective and more selective than the covalent type of resins. Column experiments allowed collection of toxic metals from sub-ppm concentrations and clear separation between favored metal ions and other ions.

Key Words: Solvent impregnated resins; Dithiophosphates; Functional polymers; Metal complexation; Cd; Pb; Cu; Ni; Polymer morphology

INTRODUCTION

Dialkyldithiophosphoric acids are known to be very powerful metal extractants (1,2). This class of extractants shows very strong affinity towards a large number of transition metal ions over a wide range of solution acidity. They also have been studied widely as efficient extractants in solvent extraction (liquid–liquid) technology (3). The extraction constant series given as log K_{Me-H} for di-(2-ethylhexyl)-dithiophosphoric acid (D2EHDTPA) [compound (**1**) in Sch. 1] in heptane from 1 *M* HCl solutions is as follows [see Ref. (1)]: Au(I) > Ag(I){40.00} > Hg(II) > Pt(II) > Pd(II) > Bi(III){19.00} > Cu(II) {12.30} > Ir(III) > As(III){11.93} > Ru(III) > In(III){10.22} > Fe(III) {8.62} > Pb(II){8.09} > Cd(II){7.01} > Sn(II){5.45} > Ni(II){3.14} > Zn(II){2.25} > Tl(I){2.00} > Co(II){0.9} > Ga(III){−1.0} > Fe(II) {−2.8} > NH_4{−3.5} > Na{−3.7}.



Scheme 1. Dialkylthiophosphoric and dialkyldithiophosphoric acids.

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The solvent extraction technique, as powerful as it is, suffers from various limitations, such as leakage of the extractant to the aqueous phase, which causes definite environmental, fear-hazard, and health-risk problems. In addition, inefficient metal recovery from very dilute metal solutions and very expensive equipment add to the limitations.

Earlier efforts from our laboratory (4–8) described the design of several types of solvent impregnated resins (SIRs) and the incorporation of the extractant D2EHDTPA into a polymeric support by a physical impregnation. These dithiophosphoric acid based SIR-immobilized polystyrene divinylbenzene (DVB)-crosslinked polymers (Amberlite XAD-2, XAD-4) show great efficiency in metal extraction, yet have several shortcomings, such as low extractant loading (5), resistance of hydrophobic polystyrene support to aqueous environment, and some D2EHDTPA leakage from the polymer phase. These require more research.

Realizing the advantage of D2EHDTPA-type SIRs, we thought it would be of sufficient interest to synthesize covalently attached dithiophosphoric acids and compare their properties with the SIR type. Several resins containing phosphinic and phosphonic acid groups have been prepared by both direct co-polymerization of phosphorus-containing monomers (9,10) and functionalization of prepared porous resins (11), but the covalent binding of dithiophosphoric derivatives has been reported only for polyvinylchloride in the study performed by our group (12), and no detailed study for beads was performed.

In this paper, we compare covalently bound dithiophosphoric ligands attached to Amberlite XE-305 with their SIR counterparts immobilized on ionic resins by ionic interactions. The results presented here show that SIR-type materials are far more efficient separation tools than their covalently bound counterparts. Furthermore, we discovered a very interesting and new phenomenon relating to the mobility of the extractants inside the ion-exchange resin matrix, which is discussed in our second paper.

EXPERIMENTAL

Materials and Reagents

2-Ethylhexanol (Merck, Darmstadt, Germany), and finely powdered P_2S_5 (BDH, Poole, UK) were used in the synthesis of D2EHDTPA. The synthesis and purification of D2EHDTPA are described in Ref. (5). *p*-Toluenesulfonyl chloride, thiophosphoryl chloride, and chlorosulfonic acid 2,4-*bis*(4-phenoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide were obtained from Aldrich (Milwaukee, WI). Phenyl dichlorothiophosphate was synthesized by the reaction of thiophosphoryl chloride with phenol according to literature (13) Anal. Calcd for

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$C_6H_5PSOCl_2$: C, 31.72; H, 2.2; P, 13.64; S, 14.13. Found: C, 31.92; H, 2.3; P, 13.43; S, 14.5.

Metal salts used were of analytical grade. All solutions were prepared using distilled deionized water (Milli-Q System, Millipore, Bedford, MA). Amberlite XAD-4, Amberlite XAD-2, and Amberlite XE-305, 2% DVB-crosslinked polystyrene resins were supplied by Rohm and Haas (Philadelphia, PA).

Divinylbenzene-crosslinked polyvinylpyridine (PVP) resin described as Reillex™ (Reily Chemicals S.A., Brussels, Belgium) and DVB-crosslinked polystyrene resins bearing weakly basic tertiary amine groups (Lewatit MP62, Bayer A.G., Leverkusen, Germany) were used.

The resin bases that were used for preparing the SIRs, their designations and properties described in this paper are given in Table 1.

Instruments

Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker DPX-250 and Bruker AMX 400 (Bruker NMR, Billerica, MA). Mass-spectrum was obtained using Finnigan Mat 4600 mass spectrometer (Thermo Finnigan, San Jose, CA). The infrared (IR) spectra from 4000 to 400 cm^{-1} were recorded with a Nicolet 460 FT-IR spectrophotometer (Thermo Nicolet, Madison, WI) (KBr pellets) and spectra from 600 to 200 cm^{-1} were recorded with a Carl Zeiss 210 double-beam spectrophotometer (Carl Zeiss, Jena, Germany) (nujol mull and polyethylene discs). Metals in the solutions were analyzed by Perkin–Elmer 5100 Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer, Shelton, CT) or by inductively coupled plasma (ICP) optical emission spectrometry using Spectro Spectroflame spectrophotometer (Spectro, Kleve, Germany).

Synthesis of Model Compounds

The synthesis of model compounds is described in Sch. 2.

N-Tosyl Diethanolamine (**1**) or Alternatively *p*-Toluene Sulfonyl Diethanolamine

p-Toluenesulfonyl chloride (*p*-tosyl chloride) (10 g, 0.05 mol) was mixed with diethanolamine (15.2 mL) in 50 mL of chloroform. After 12 hr, the organic phase was washed with cold water followed by 5% solution of $NaHCO_3$ (50 mL), then dried over sodium sulfate. The chloroform was removed by distillation under vacuum to yield a white solid (89% yield). ^1H NMR δ ($CDCl_3$, 250 MHz) =

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Table 1. Resins' Description and Properties

Trademark	Basicity	Ion Exchange Capacity (meq/g)	N Content by Elemental Analysis (meq/g)	Dry State Surface Area (m^2/g)	Swollen State Pore Volume (cm^3/g)	Average Pore Diameter (Å)	Divinylbenzene (DVB) Content (mol%)
Reillex HP	Weak	5.2	6.0	76	0.872	—	25[a]
Lewatit MP62	Weak	5.2	5.5	14	0.270	—	n.s.
Amberlite XAD-2	—	—	—	340	0.65	90	n.s.
Amberlite XAD-4	—	—	—	804	—	50	n.s.
Amberlite XE-305	—	—	—	48	—	1400	2

[a] Information was supplied by manufacturer.
n.s. not specified.

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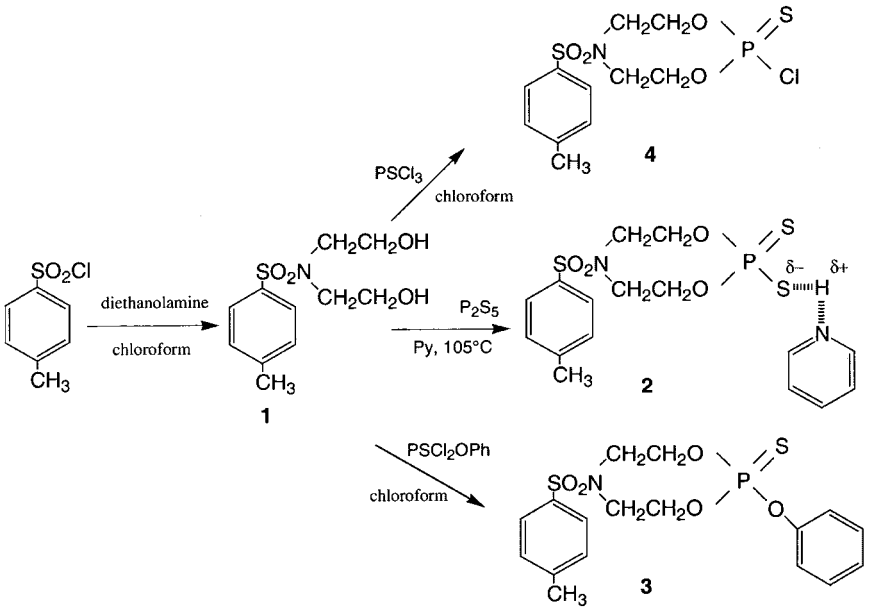


Scheme 2. Synthesis of model compounds.

7.70 and 7.33 (4H, two doublets, $J = 8.26$ and 8.02, $CH_3-C_6H_4-S$); 4.82 (2H, singlet, $(OH)_2$); 3.85 (4H, triplet, $J = 4.83$, $(-N-CH_2-CH_2-O-)_2$); 3.25 (4H, triplet, $J = 4.85$, $(-N-CH_2-CH_2)_2$); 2.43 (3H, singlet, $CH_3-C_6H_4-S$). IR: 3245.2 cm^{-1}, ν(OH); 1337.5 and 1162.4 cm^{-1}, $\nu(SO_2$ of sulfonamide); 1087.1 cm^{-1} ν(C–O) of alcohol. Anal. Calcd for $C_7H_9SNO_4$: C, 32.42; H, 3.47; S, 12.37; N, 5.4. Found: C, 32.52; H, 3.49; S, 12.07; N, 5.31.

2-Hydrothioxy-2-thio-6-(*p*-tosyl)-1,3,6,2-dioxaazaphosphacyclooctane · Pyridine Complex (**2**)

Under a nitrogen atmosphere, P_2S_5 (0.45 g, 0.002 mol) was dissolved in 50 mL of dry pyridine at 105–110°C. *p*-Toluene sulfonyl diethanolamine (**1**) (0.5 g, 2 mmol) was added to the solution with stirring. The mixture was maintained at 105°C for 3 hr, then pyridine was removed by distillation, and the product was extracted with toluene and precipitated by the addition of hexane to the toluene solution. Thus, the product was obtained as white crystals in 85% yield, m.p. 158–160°C. ^{1}H NMR δ ($CDCl_3$, 400 MHz) = 9.07 (2H, doublet, $J = 8.36$, pyridine); 8.40 (1H, triplet, $J = 12.45$, pyridine); 7.95 (2H, triplet,

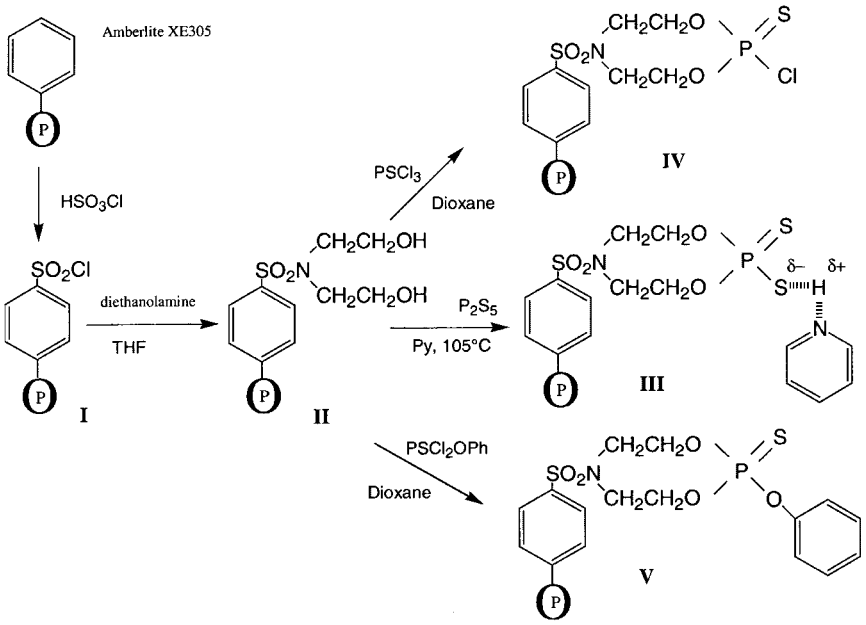
$J = 9.8$, pyridine); 7.71 and 7.35 (4H, two doublets, $J = 13.1$ and 12.78 $CH_3-C_6H_4-S$); 4.38–4.27 (4H, multiplet, $(-N-CH_2-CH_2-O-)_2$); 3.47 (4H, triplet, $J = 7.59$ $(-N-CH_2-CH_2-O-)_2$); 2.44 (3H, singlet, $CH_3-C_6H_4-S$) and ^{31}P NMR δ ($CDCl_3$, 400 MHz) = 59.4 (1P, singlet). IR: 1334.5 and 1158.9 cm^{-1}, $\nu(SO_2$ of sulfonamide); 1055.7, 1042.5, 992.3, and 965.2 cm^{-1} $\nu((C-O)$ of [C–O]–P); 760.1 and 745.1 cm^{-1} $\nu((P-O)$ of C–[O–P]); 684.1 cm^{-1} $\nu(P = S)$. Anal. Calcd for $C_{16}H_{21}S_3NPO_4$: C, 44.4; H, 4.86; N, 6.47; S, 22.25; P, 7.16. Found: C, 44.2; H, 5.03; N, 6.46; S, 21.7; P, 7.02.

2-Phenoxy-2-thio-6-(*p*-tosyl)-1,3,6,2-dioxaazaphospha Cyclooctane (**3**)

p-Toluene sulfonyl diethanolamine (**1**) (3.1 g, 0.012 mol) was dissolved in dry chloroform, mixed with triethylamine (3.3 mL, 0.024 mol), and then phenyl dichlorothiophosphate (1.93 mL, 0.012 mol) was added dropwise. After 6 hr, the reaction mixture was washed 2–3 times with NaH_2PO_4 aqueous solution (pH = 4.3) to remove chlorohydrate of triethylamine. The organic phase was dried over sodium sulfate. After chloroform was removed, the product (white solid) was recrystallized from toluene (90% yield). ^1H NMR δ ($CDCl_3$, 400 MHz) = 7.75 (2H, doublet, $J = 8.28$, $CH_3-C_6H_4-S$); 7.40–7.38 (4H, multiplet, $CH_3-C_6H_4-S$ and $-O-C_6H_5$); 7.31–7.26 (3H, multiplet, $CH_3-C_6H_4-S$); 4.63–4.38 (4H, multiplet, $(-N-CH_2-CH_2-O-)_2$); 3.54 (4H, triplet, $(-N-CH_2-CH_2)_2$) 2.49 (3H, singlet, $CH_3-C_6H_4-S-$) and ^{31}P NMR δ ($CDCl_3$, 400 MHz) = 62.4 (1P, singlet). IR: 1338.3 and 1157.7 cm^{-1} $\nu(SO_2$ of sulfonamide); 1046.6, 1008.7, 972.8, and 953.7 cm^{-1} $\nu((C-O)$ of [C–O]–P); 805.2 and 777.0 cm^{-1} $\nu((P-O)$ of C–[O–P]); 688.3 cm^{-1} $\nu(P = S)$. Anal. Calcd for $C_{17}H_{20}S_2NPO_5$: C, 49.42; H, 4.84; N, 3.39; S, 15.53; P, 7.49. Found: C, 49.6; H, 4.79; N, 3.37; S, 15.12; P, 7.31.

2-Chloro-2-thio-6-(*p*-tosyl)-1,3,6,2,-dioxaazaphospha Cyclooctane (**4**)

An amount of 1.3 g (0.0075 mol) of thiophosphoryl chloride was added to a mixture of 1.9 g (0.0075 mol) of compound (**1**) and 1.56 g (0.015 mol) of triethylamine in 40 mL of tetrahydrofuran (THF). After 6 hr, THF was evaporated, and the product was separated from yellow oil by washing with toluene. The solution of the resulting product in toluene was concentrated and precipitated with hexane as white crystals (88% yield). m.p. 137–138°C. ^1H NMR, δ ($CDCl_3$, 400 MHz) = 7.68 and 7.34 (4H, two doublets, $J = 8.4$ and $J = 8.0$, $CH_3-C_6H_4-S$); 4.58–4.35 (4H, multiplet, $(-N-CH_2-CH_2)_2$); 3.57–3.37 (4H, multiplet, $(-N-CH_2-CH_2)_2$); 2.45 (3H, singlet, $CH_3-C_6H_4-$) and ^{31}P NMR δ ($CDCl_3$, 400 MHz) = 71.6 (1P, singlet). IR: 1336.4 and 1164.6 cm^{-1} $\nu(SO_2$ of sulfonamide); 1027.7, 1006.9, 998.5 (shoulder), and 971.6 cm^{-1} $\nu((C-O)$ of [C–O]–P); 795.1 and 779.7 cm^{-1} (shoulder) $\nu((P-O)$ of C–[O–P]);



Scheme 3. Synthesis of functional polymers (**III**)–(**V**).

660.5 cm^{-1} ν(P = S)). Anal. Calcd for $C_{11}H_{15}S_2NPO_4Cl$: C, 37.12; H, 4.22; P, 8.71. Found: C, 36.98; H, 4.36; P, 8.82. Mass spectrum: $M^+ = 355$, $(M+2)^+ = 357$; with isotopic ratio of ^{35}Cl- and ^{37}Cl-containing isotopomers equal to 2.8:1.

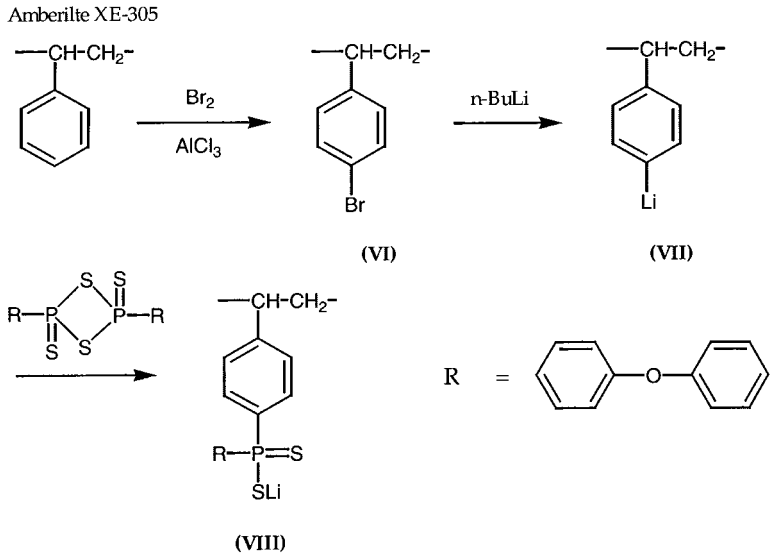
Preparation of Solvent Impregnated Resins

Solvent impregnated resins on nonfunctional polymeric supports (Amberlite XAD-2 and XAD-4) were prepared according to literature (5). Solvent impregnated resins on functional polymeric supports (Reillex HP and Lewatit MP resins) were made by the same procedure as literature (7).

Synthesis of Functional Polymers (Schs. 3 and 4)

Chlorosulfonated Amberlite XE-305 (**I**)

An amount of 5.7 g of Amberlite XE-305 was swollen in the mixture of dry methylene chloride (50 mL), 1,2-dichloroethane (50 mL), and chlorosulfonic acid



Scheme 4. Synthesis of functional polymers (**VII**) and (**VIII**).

(4.98 mL), then the polymer slurry was stirred gently overnight. Chlorosulfonated polymer was separated and washed with dry methylene chloride and ethyl acetate, then finally with THF. IR: 1372.5 and 1169.9 cm^{-1} $\nu(SO_2$ of sulfochloride). Anal. Found: S, 14.28; Cl, 15.62 (4.4 mmol/g).

bis(2-Hydroxyethyl)aminosulfonyl-XE305 [Modified Polymer (**II**)]

Chlorosulfonated resin (**I**) (6.73 g) was shaken with diethanolamine (4.67 mL) dissolved in the THF solution for two days, then separated and washed with methanol. The polymer was dried under vacuum. IR: 3387.4 cm^{-1} ν(OH); 1330.3 and 1158.2 cm^{-1} $\nu(SO_2$ of sulfonamide); 1038.1 cm^{-1} ν(C–O) of alcohol. Anal. Found: N, 4.41 (3.15 mmol/g); Cl, 0.4.

2-Mercapto-2-thioxo-1,3,6,2-dioxaazaphosphacyclooct-6-yl-sulfonyl-XE305 Pyridine Complex [Modified Polymer (**III**)]

Polymer (**II**) (1.73 g, 0.0062 mol) was added to the pyridine solution of phosphorous pentasulfide (2.07 g, 0.0093 mol) at 105–110°C. The polymer slurry was heated and stirred gently for 24 hr. The resulting polymer was separated and

washed by refluxing with pyridine in soxhlet apparatus for two days, and then dried under reduced pressure. IR: 1330.4 and 1157.1 cm^{-1} $\nu(SO_2$ of sulfonamide); 1055.9, 1036.4, 1004.9 (shoulder), 991.9, and 963.3 cm^{-1} ν((C–O) of [C–O]–P); 774.4 and 741.6 cm^{-1} (ν(P–O) of C–[O–P]); 683.0 cm^{-1} ν(P = S). Anal. Found: P, 4.01 (1.29 mmol/g).

2-Chloro-2-thioxo-1,3,6,2-dioxaazaphosphacyclooct-6-yl-sulfonyl-XE305 [Modified Polymer (**IV**)]

To polymer (**II**) (1 g, 0.0036 mol) swollen in dioxane, 0.61 g (0.0036 mol) of thiophosphoryl chloride and 0.75 g (0.0074 mol) of triethylamine were added. The reaction mixture was left overnight with gentle stirring. Then, another set of equivalent portions of thiophosphorylchloride (Aldrich) and triethylamine was added. After ca. 12 hr the polymer was separated and washed with dioxane, followed by THF, and then dried under vacuum. IR: 1334.6 and 1159.9 cm^{-1} $\nu(SO_2$ of sulfonamide); 1027.4, 1006.7, 998.9, and 966.6 cm^{-1} (ν(C–O) of [C–O]–P); 792.3 and 779.7 cm^{-1} (shoulder) (ν(P–O) of C–[O–P]); 667.4 cm^{-1} ν(P = S). Anal. Found: P, 6.41 (2.07 mmol/g); Cl, 7.34.

2-Phenoxy-2-thioxo-1,3,6,2-dioxaazaphosphacyclooct-6-yl-sulfonyl-XE305 [Modified Polymer (**V**)]

Polymer (**V**) was prepared according to the procedure followed in polymer (**IV**) preparation using phenyl dichlorothiophosphate instead of thiophosphorylchloride. IR: 1331.2 and 1157.9 cm^{-1} $\nu(SO_2$ of sulfonamide); 1037.9, 1009.8, 988.0, and 952.1 cm^{-1} (ν(C–O) of [C–O]–P); 805.5 and 779.2 cm^{-1} (shoulder) (ν(P–O) of C–[O–P]); 684.2 cm^{-1} ν(P = S). Anal. Found: P, 5.14 (1.66 mmol/g).

Synthesis of Polymer **VIII** Via Bromination of XE-305 and Lithiation (see Sch. 4) Brominated 2% Divinylbenzene-Crosslinked Polystyrene Resin, Amberlite XE305 (**VI**)

The bromination was performed according to literature (14). Anal. Found: Br, 40.82 (5.1 mmol/g).

4-(*p*-Phenoxyphenyl(mercapto) Thiophosphoryl-XE305 [Polymer (**VII**)]

A brominated resin (**VI**) (2.07 g, 10.4 mmol Br) was swollen in 60 mL of dry benzene, then 10 mL of 2.5 *M* *n*-BuLi dissolved in hexane was added. After

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3 hr at 60°C, the solvent was removed and the polymer was washed with dry THF twice. Then 4.3 g (0.0081 mol) of 2,4-*bis*(4-phenoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide dissolved in THF was added in small portions using a syringe, and the reaction was kept overnight at room temperature. All procedures were performed in an inert atmosphere of argon. The resulting polymer was washed repeatedly with dioxane–water (10:1) and THF. ^{31}P MAS solid-state NMR δ (THF, 300 MHz) = 65.4 (1P, singlet); 6.63 (1P, singlet, weak). IR: 679.0 cm^{-1} ν(P = S). Anal. Found: P, 5.57 (1.8 mmol/g).

Extraction Procedure

Polymer samples (0.5–1.0 g) were slurry-packed in Pyrex glass columns fitted with a sinter glass filter and Teflon stopcock. The resin-bed volumes were about 7 mL in each column. Columns were pretreated with perchloric acid of the same concentration as in the metal solution that was passed later in the column. Then, metal-containing aqueous solutions in $HClO_4$ at a desired pH were passed through the column (1.0 mL/min) until the metal concentration in the effluent solution was equal to that in the influent solution (equilibrium situation). The column was then washed with water, and the metal ions were recovered by elution with 0.2 *M* ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (EDTA) solution in ammonia (pH = 9.4; 150 mL, 1.0 mL/min). The metal and phosphorous concentrations in the effluent solution were measured using ICP "Spectro" or Perkin–Elmer 5100 AAS. On the basis of collected data, the breakthrough and elution curves were plotted, and metal adsorption capacities were calculated.

RESULTS AND DISCUSSION

Functional Polymers

Following the model reactions shown in Sch. 2, the modified polymer (**II**) containing diethanolsulfonamide group was prepared on the basis of Amberlite XE-305 resin (Sch. 3) according to literature (15). This polymer allows the synthesis of various thiophosphoric functionalities. Two synthetic pathways were chosen to obtain dithiophosphoric groups on the polymer. The first method leading to polymer (**III**) is essentially an analogy of the common method of dialkyldithiophosphoric acids synthesized by heterogeneous reaction of alcohols with P_2S_5 (5). The principle adaptation in the synthesis procedure is due to the fact that P_2S_5 must be dissolved in an appropriate solvent that also allows the reacting polymer to possess good swelling characteristics in this solvent. We

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found that pyridine matches all these demands and, hence, the synthesis was successful. All reactions taking place on the polymers were verified first on soluble model analogs of the polymers (Sch. 2). The model synthesis is essential for evaluating the modified polymer chemical structure by comparing the IR spectra of the polymer and its soluble analogs. While the structure of the model compound can be determined easily by NMR, mass spectrometry (MS), or IR spectroscopy, the structure of the insoluble crosslinked polymer is obtained only from IR spectroscopy. A detailed analysis of the IR spectra of both molecular and polymer analogs in 1640–1600, 1400–900, and 800–600 cm^{-1} regions was used to provide proof of the chemical structure of the immobilized reactive groups on the polymer.

The second method via polymer (**IV**), was ineffective due to the unexpected resistance of polymer (**IV**) to thiolation. Until now, it was not possible to convert the chloroanhydride to a dithiophosphoric acid with the use of NaSH as the thiolating agent. Attempts to introduce an SH group by reaction with compound (**4**) in a similar way were not successful.

Polymer (**II**) can be used for immobilization of various thiophosphorous derivatives, e.g., polymer (**V**).

The synthesis of the crosslinked polymer containing dithiophosphinic acid group was carried out on commercial polystyrene Amberlite XE-305 polymer (Sch. 4). The modified polymer adsorbs heavy metal ions such as Pb(II) (0.48 mmol/g) and Cd(II) (0.31 mmol/g). However, the resin-regeneration step is quite problematic and the resin metal adsorption performance drops considerably (about 30%) already in the second adsorption cycle. A reasonable explanation might be that dialkyldithiophosphoric acids are very strong extractants for heavy metals. Consequently, such metal ions cannot be stripped easily under mild conditions and therefore stronger complexing agents like concentrated mineral acids or EDTA at basic pH will be required. In addition, some of the dithiophosphoric acid groups are hydrolyzed and cannot be effective for a second metal-extraction cycle.

Additional attempts to introduce the dithiophosphinic functionality chemically into the polymer included reacting Amberlite XE-305 resin with thiophosphoryl chloride. The modified polymers were identified by elemental analysis, which has indicated that thiophosphoryl chloride reacts mostly via two chlorine atoms. (The third chlorine atom is much less reactive than the other two.) This reaction provides an additional crosslinking of the resin. Subsequent reaction with H_2S did not cause a substantial decrease of the chlorine content of the resulting polymer. Thus, our attempts at polymer thiolation were unsuccessful.

We have therefore concluded that SIR type is far more superior to the covalently bound dithiophosphoric acid resins and conducted separation experiments mainly on the SIR type.

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Solvent Impregnated Resins: Spectral Characterization of the Metal Complexes

The metal-extraction process was followed using mainly IR spectroscopy. In the IR spectra of Reillex HP based SIRs, there are three regions in which characteristic absorption bands can be found: (a) 2800–2500 cm^{-1}, ν[PyN···H]$^+$—strong, broad band; 2595 cm^{-1}, ν[S–H]—very weak and sharp; 2070 cm^{-1}, ν[S–H]···NPy—weak; (b) 1637–1417 cm^{-1}, absorption of pyridine groups of Reillex HP (absorption at 1600 cm^{-1} corresponding to the unsubstituted pyridine group, and absorption at 1636 cm^{-1} corresponding to either D2EHDTPA-complexed or protonated pyridine); 1380–1350 cm^{-1} NO^{-3} absorption—very strong; (c) 1006 cm^{-1} [O_2–P]–S—intense; 877 cm^{-1}, O_2–[P–S]—weak; 678 cm^{-1} ν[P = S]—intense. The actual mechanism of the complexation process was verified with the aid of *elution experiments*. Even organic solvents cause the extractant (D2EHDTPA) to be eluted only to a very small degree from the impregnated Reillex HP polymer. The ratio between free (1600 cm^{-1}) and protonated (1636 cm^{-1}) pyridine ring peaks remains almost unchanged. On the other hand, the metal complex of D2EHDTPA elutes very readily. The D2EHDTPA complexes of several metals, including Cu, Pb, and Cd, were eluted from the respective SIRs with methanol. The UV spectra of the eluted Cu-D2EHDTPA, Ag-D2EHDTPA, and Ni-D2EHDTPA complexes (420, 362, and 390 nm, respectively) were identical to the CuL_2, AgL_2, and NiL_2 complexes previously prepared in *n*-hexane. The SIR samples were washed with methanol and dried, then IR spectra were recorded.

Solvent impregnated resins loaded with two different kinds of metals were investigated (Fig. 1): (1) SIRs complexing a metal (Pb) that forms very weak complexes with the pyridine groups of Reillex resin and (2) SIRs complexing metals (Cu, Ag) that form strong complexes with both D2EHDTPA and the pyridine groups of Reillex HP resin.

The spectrum [Fig. 1(**2**), c], of an SIR after Cu-D2EHDTPA complex elution, is very similar to the spectrum of the Reillex HP resin after Cu(II) extraction [Fig. 1(**2**), a], but two bands arising from stretching vibrations of the pyridine complex ν[PyN···H]$^+$ at 2800–2500 cm^{-1} and the protonated pyridine ring at 1636 cm^{-1} still remain in the washed resin sample. The IR spectrum of the SIR after elution of the Pb–D2EHDTPA complex [Fig. 1(**1**), d] contains a ν[PyN···H]$^+$ band at 2800–2500 cm^{-1}, protonated pyridine ring absorption at 1637 cm^{-1} and NO_3^- ion peak at 1384 cm^{-1}. Furthermore, the bands assigned to D2EHDTPA absorption (e.g., the intense 660 and 1006 cm^{-1} bands) were not observed. The NO_3^- peak cannot be a result of Pb complexation by Reillex HP polymer [Fig. 1(**1**), b] and must, therefore, be related to the pyridine group protonation process.

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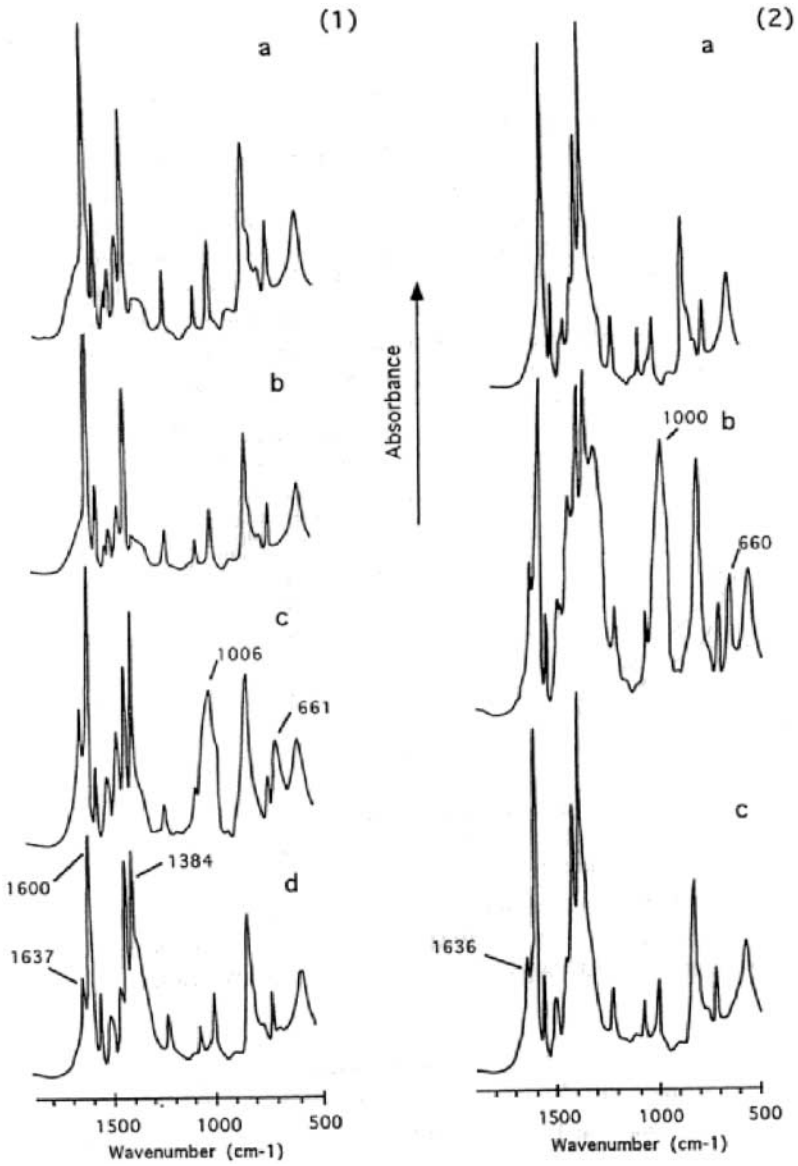

Figure 1. Infrared spectra of Reillex HP resins and Reillex HP based SIRs. (1) Reillex HP resin (a); Reillex HP resin after Pb(II) extraction (b); Reillex HP Based SIR after Pb(II) extraction (c); Reillex HP based SIR after Pb(II) extraction washed with MeCN (d). (2) Reillex HP resin after Cu(II) extraction (a); Reillex HP based SIR after Cu(II) extraction (b); Reillex HP based SIR after Cu(II) extraction washed with MeCN (c).

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Comparison of Metal Ion Extractions by Functional Polymers with Solvent Impregnated Resins

The ability of the functional polymer (**III**) to adsorb selectively the metal ions from aqueous solutions has been evaluated in comparison with Reillex HP based SIRs containing D2EHDTPA as a metal extractant. Infrared spectra of functional polymer (**III**) and Reillex HP based SIR before and after metal extraction are shown in Fig. 2. It can be seen clearly that $\nu(P=S)$ characteristic absorption band is shifted with metal adsorption, and this shift is comparable with a shift of $\nu(P=S)$ peak for D2EHDTPA–metal complex formation on SIR.

Since the D2EHDTPA extractant is known to have higher affinity for heavy and "soft" metal ions, we decided to test the "selectivity profile" of the D2EHDTPA type and at the same time compare the SIR type with covalently bound type resins. This was done by contacting the resins with an aqueous solution containing 20 metal ions.

Figure 3 shows the results of this experiment: a profile of metal extraction. Indeed, for a functional resin (**III**) [Fig. 3(a)] and the D2EHDTPA–SIR analog [Fig. 3(b)]. Both resins show, as expected, selectivity for Ca over Cu, Cd, Pb, and Ni, but the SIR-type resin is much more effective in reducing the metal concentrations to lower levels.

Column Metal Extraction and Selective Metal Separation

Aqueous solutions of individual metals, Pb(II), Cd(II), Ni(II), Zn(II), and Au(II), or some of their mixtures were passed through columns containing Reillex HP polymer, Amberlite XAD-4 based SIRs, and polymer (**III**), respectively. The results of these experiments are given in Table 2. The results shown indicate metal capacities of 0.4–0.6 mmol/g of resins for the four metals (Ni, Cd, Zn, Pb) based on SIRs and polymer (**III**).

Frontal analysis of mixtures of Pb/Zn and Pb/Ni are shown in Ref. (7). To determine the selectivity factors, the metals were eluted and the solutions were analyzed by atomic absorption. The separation factors α given in Table 2 are in excess of 1000 and were calculated by use of the following expression:

$$\alpha_{M1}^{M2} = \frac{Y_{M2}}{Y_{M1}} \frac{X_{M1}}{X_{M2}} \tag{1}$$

where Y and X are the equivalent fractions of ions under separation in the resin and solution phases, respectively; indices 1 and 2 are chosen so that $\alpha > 1$.

As can be seen from Table 2, separation factor values for Cd/Zn, Pb/Zn, and Cd/Ni ion pairs are too high to be measured exactly and practically independent of

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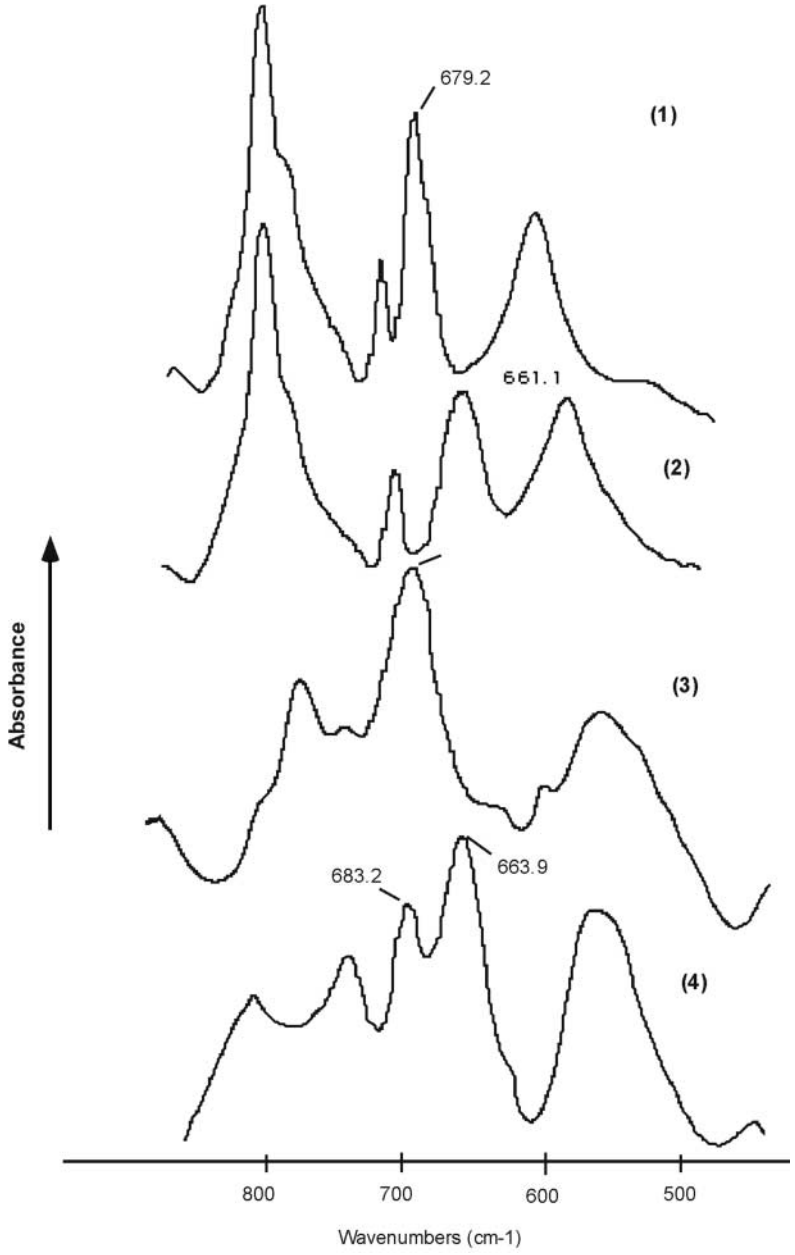

Figure 2. Infrared spectra of (1) D2EHDTPA on Reillex HP; (2) D2EHDTPA–Pb(II) complex on Reillex HP; (3) polymer (**III**); (4) polymer (**III**) after Pb(II) extraction.

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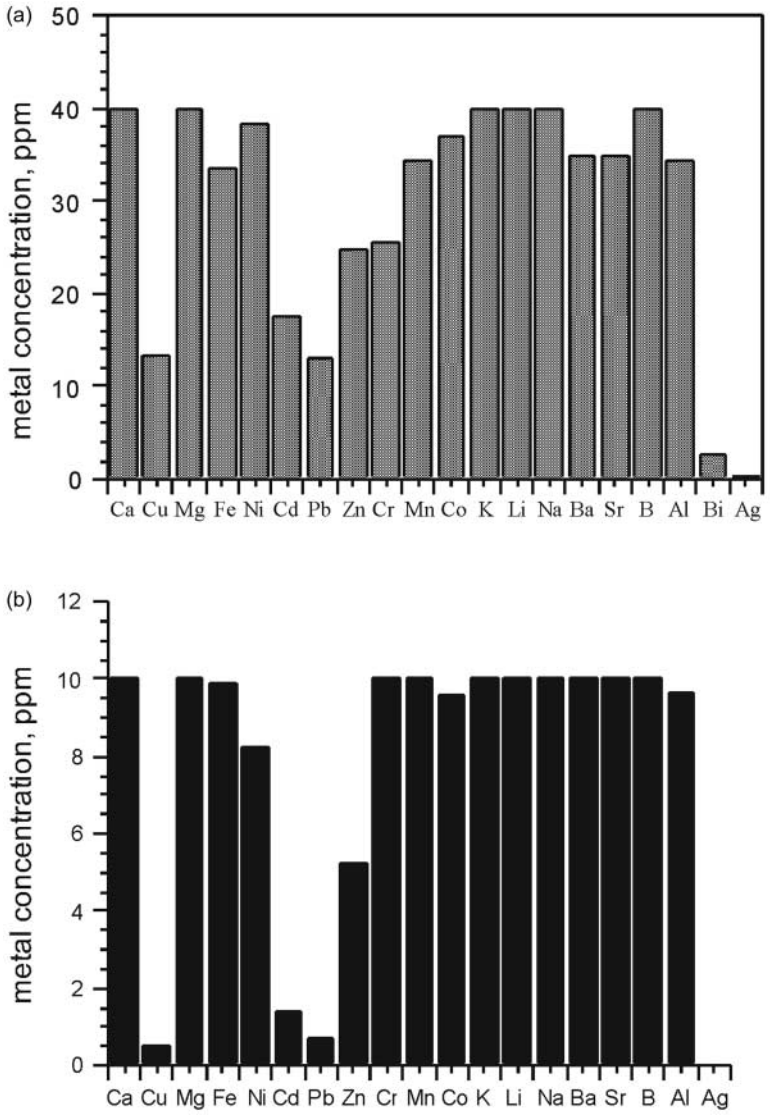

Figure 3. (a) Selective metal sorption from 0.1 *N* nitric acid solution on modified polymer (**III**). (b) Selective metal sorption on Reillex HP based SIR, loading 0.2 g D2EHDTPA/g of SIR (nitric acid).

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Table 2. Metal Extraction with Solvent Impregnated Resins (SIRs) on Different Polymeric Supports and Chemically Modified Polymers

Resin	Feed Solution $HClO_4$ Concentration (mol/L)	Metal Concentration in Feed Solution (mmol/L)	Resin Loading with D2EHDTPA (mmol/g of Support)	Total Metal Capacity[a] (mmol/g of Support)	Utilization of the Supported Extractant[b]	Separation Factor[a]
Reillex HP based SIR	Neutral	4.02 Cd(II) 3.10 Zn(II)	1.50	0.60	81	$\gg 1000$
Reillex HP based SIR	0.1	3.29 Cd(II) 5.08 Zn(II)	1.51	0.63	84	$\gg 1000$
Reillex HP based SIR	1	4.07 Cd(II) 5.04 Zn(II)	1.49	0.67	90	$\gg 1000$
Reillex HP based SIR	5	3.30 Cd(II) 5.35 Zn(II)	1.35	0.60	89	$\gg 1000$
Reillex HP based SIR	0.1	4.30 Pb(II) 5.0 Zn(II)	1.49	0.63	84	$\gg 1000$
Reillex HP based SIR	1	4.1 Cd(II) 4.28 Ni(II)	1.44	0.65	89	$\gg 1000$
Reillex HP based SIR	1	4.06 Cd(II) 4.42 Pb(II)	1.49	0.64	85	9.8
Reillex HP based SIR	Neutral	0.2 Pb(II)	—	0.01	—	—
Reillex HP based SIR	Neutral	1.0 Pb(II)	1.1	0.44	80	—
Polymer (**III**)	0.1	1.8 Cd(II)	1.52[d]	0.41	54	—
Polymer (**III**)	0.1	0.96 Pb(II)	1.52[d]	0.48	63	—
Polymer (**III**)	0.2[c]	0.51 Au(II)	1.52[d]	0.38	50	—
Polymer (**III**)	0.2	1.57 Cu(II)	1.52[d]	0.42	55	—
AmberliteXAD-4 based SIR	0.1	0.62 Pb(II)	0.93	0.089	19	—
Amberlite XAD-2 based SIR	0.1	0.2 Pb(II)	0.54	0.15	55	—

[a] Obtained from elution data.
[b] Supposing ML_2 stoichiometry.
[c] Solution in HCl.
[d] Functional groups calculated by P content.

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perchloric acid concentration. The value of separation factor α_{Cd}^{Pb} of Reillex HP based SIR is similar to the value (12.02) found in solvent extraction experiments with D2EHDTPA solutions in heptane (1). The capacity of SIRs based on the Reillex HP was remarkably higher than that observed with porous polystyrene DVB-crosslinked resin (Amberlite XAD-4) based SIR at nearly the same D2EHDTPA loading and with modified polymer (**III**). A possible explanation of this phenomenon is the restricted access of metal ions to the polymer reactive sites due to hydrophobicity of polystyrene-based resins in which the extractant exists as a separate phase occupying the pore volume. The contrary is observed for all SIRs based on Reillex HP polymeric support having most or all active D2EHDTPA groups. This is an indication of the high accessibility of D2EHDTPA molecules adsorbed in the polymer matrix of the basic supports. Di-(2-ethylhexyl)-dithiophosphoric acid concentration in column effluent solutions was evaluated on the basis of ICP analysis of the phosphorous content. It was found that for the SIRs based on Reillex HP the extractant leakage seems to be negligible, as the phosphorous concentration in effluents was lower than 0.02 ppm.

Removal of Cadmium from Very Dilute Solutions

Selective Cd(II) recovery experiments were carried out from the metal perchlorites mixtures. The composition of solution used was as follows: Cd(II) (4.07 mmol/L), Zn(II) (5.04 mmol/L), Ni(II) (4.28 mmol/L), Na(I) (41.3 mmol/L), Mg(II) (36.1 mmol/L), and Ca(II) (20.2 mmol/L). These metals are always present in tap water. The results of the column separations at different perchloric acid concentrations are summarized in Table 2. The results of the stripping solution analysis (metal complexes were stripped with MeOH) showed the presence of only Cd(II) ions. It means that the separation factor values are too high to be determined.

The examination of Lewatit MP-62-D2EHDTPA resin for its extraction ability of trace amounts of Cd(II) (Fig. 4) and Pb(II) (not shown in Fig. 4) from an ordinary matrix of other elements (tap water), shows the high efficiency and selectivity of the SIR based on anion-exchangers. This test proved the possibility to lower the Cd(II) concentrations in ordinary tap water (without any pretreatment) from 100 to 2–15 ppb (with a resin-bed volume of 7.2 mL, and at a flow rate of 30 cm^3/min (about 4 BV/min) and to lower the Pb(II) concentrations from 100 to 2–10 ppb at a flow rate of 10 cm^3/min. These metal concentrations approach the Israel drinking water standards: 5 ppb for Cd(II) and 10 ppb for Pb(II).

These experiments show conclusive examples of the possible practical use of D2EHDTPA-ion-exchanger SIRs for selective extraction of heavy metals from relatively concentrated solutions or final water polishing and removal of traces of heavy metals.

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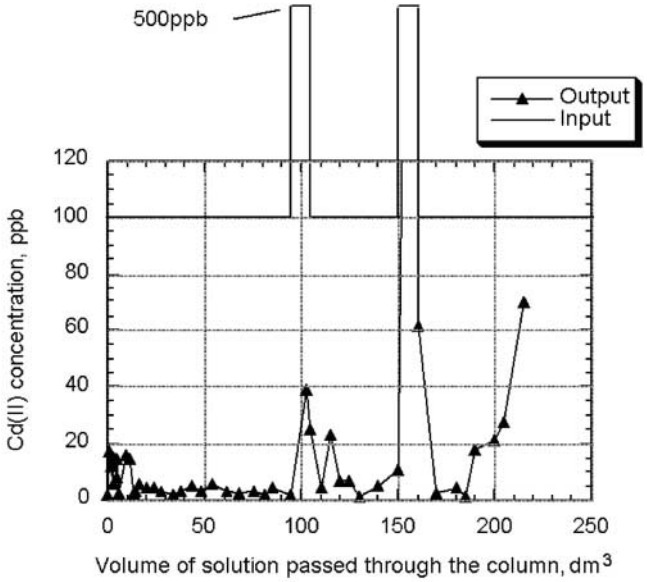

Figure 4. Removal of Cd from 100 ppb down to < 1 ppb by Lewatit MP-62-D2EHDTPA column (SIR loading 0.61 g/g of SIR, resin weight: 1.82 g; ligand leakage: < 0.2 ppm D2EHDTPA).

COMMENTS ON ELUTION

One of the key questions in ion-exchange processing of metals is the question of resin recycle. The results from Table 3 show the possibility, yet D2EHDTPA forms very strong metal complexes, therefore, SIRs based on this extractant are hard to regenerate. However, D2EHMTPA or D2EHPA (structure: see Introduction section) forms rather weak complexes with metals, and it is possible to free the metal ions by washing with mineral acids and then regenerate the extractant. In a column experiment, SIR prepared by impregnation of Lewatit MP-62 with D2EHMTPA (0.77 mmol/g) adsorbed in a column experiment 0.27 mmol Cd/mmol of supported extractant from 0.013 *M* solution of cadmium sulfate. After regeneration by washing with 3 *M* hydrochloric acid followed by pH = 4–5 aqueous solution, the sorption capacity was found to 0.10 mmol Cd/mmol of supported ligand. After second regeneration, the capacity of 0.13 mmol Cd/mmol of supported extractant was obtained.

Metal sorption equilibrium (Eq. (1)) provides a simple way for metal elution and SIR regeneration. We will discuss this option in another paper on the topic of extraction migration inside porous ion-exchange media.

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Table 3. The Results of Cd(II) Separation on Reillex HP-Di-(2-ethylhexyl)-dithiophosphoric Acid (D2EHDTPA) Resin

Feed Solution $HClO_4$ Concentration (mol/L)	First Cycle		Second Cycle		Third Cycle	
	D2EHDTPA Loading (mmol/g of Support)	Total Cd(II) Capacity (mmol/g of Support)	D2EHDTPA Loading (mmol/g of Support)	Total Cd(II) Capacity (mmol/g of Support)	D2EHDTPA Loading (mmol/g of Support)	Total Cd(II) Capacity (mmol/g of Support)
0.1	1.51	0.81	1.39	0.65	1.38	0.63
1	1.49	0.72	1.45	0.76	1.42	0.70
5	1.35	0.68	1.50	0.75	1.43	0.70

Flow rate was set to 3 cm^3/min after Cd(II) metal complex was stripped with MeOH, SIRs were treated with 2 *M* HNO_3 followed by the washing with 2 *M* NaOH and water.

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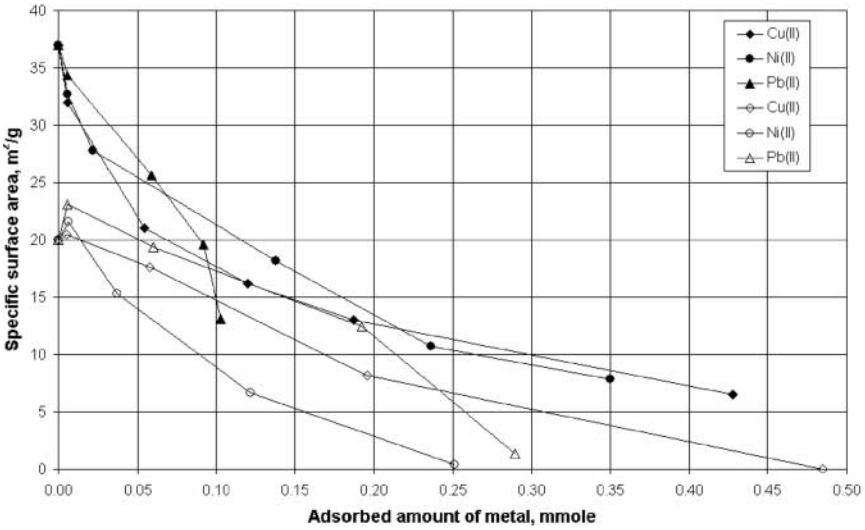

Figure 5. Polyvinylbenzene-M based SIR (filled symbols) and LEW-Mw based SIR (open symbols) surface area dependence on adsorbed amount of metal. Solvent impregnated resin loadings 0.35 g/g of SIR and 0.45 g/g of SIR, respectively.

CONCLUSIONS

1. Functional thiophosphate ester polymers may be synthesized readily by polymer analogous reactions using P_2S_5 in pyridine (Schs. 2 and 3).
2. Comparison of metal-binding properties shows similarities in metal-binding selectivity, but superior extraction properties of the SIR-type polymer [Fig. 3 and literature (7)]
3. Comparison of PVP (Reilex HP, SIRs) and poly(vinylbenzyl ammonium SIRs, Lawatite MP-62) shows superiority of the latter product's supports in metal-binding efficiency (Fig. 5).
4. Solvent impregnated resins are extremely selective in the complexation of Cd and Pb over Zn (separation factors over 1000, Table 2).

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