Approaches Toward Synthesizing Novel Extractant Systems: Polymeric Bifunctional Extractants with Synergistic Possibilities

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Approaches Toward Synthesizing Novel Extractant Systems: Polymeric Bifunctional Extractants with Synergistic Possibilities

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ABSTRACT

The synthesis of a monoarylphosphinic acid - diarylphosphine oxide extractant system supported on macroporous polystyrene beads is reported. The bifunctional resin was used in separate zinc and copper(II) ion extraction studies. Results wth both metals show an excellent extent of extraction under low loading conditions and solution pH of 1-2; at equivalent metal:resin concentrations, the resin absorbs 50% of the metal in solution. Comparison with lower absorption values reported in the literature for similar systems suggests the possibility of a synergistic extraction due to cooperation between the acid and oxide moieties.

INTRODUCTION

Systems set up to extract metal ions from a water solution

can consist of an organic solvent (diluent) in which is dissolved

1715

one or more extractants, of undiluted extractants, or of solid
polymeric materials to which are attached functional groups. A
great deal of attention has been and is being focused (1,2) on
varying the functionality and structure of the extractant in the
search for diluent-soluble reagents that will quantitatively
remove a given metal ion from an aqueous solution at a rapid
rate, will be specific for the given metal ion in the presence of
other ions under easily adjusted conditions, and can be
commercially produced. Less attention appears to have been given
to increasing the versatility of solid polymeric extractants.

The advantages of utilizing liquid extractants are well
known (3). They include the wide range of reagents available for
practically all metal ions, the ease with which an industrial
plant can be converted from recovering one metal to another by
simply changing the extractant feed stream, and the ease with
which the metal can be stripped from the extractant allowing for
quantitative recovery. Perhaps most advantageous is the ease
with which the extraction process can be controlled by changing
the process variables: dissolving the extractant in different
diluents, at different concentrations, or with additional solvat-
ing reagents.

Ligands usually utilized in liquid extractants can also be
placed onto a polymeric backbone to yield a solid reagent which
serves as both diluent and extractant. Such systems are well
known in the form of resin "ion exchangers." The use of
polymeric (or solid) extractants has its own set of advantages
that include virtually total insolubility and nonentrainment in
the aqueous phase and often a low rate of physical degradation.
For these reasons, such solid polymeric extractants are often to
be preferred where aqueous source solutions are very dilute,
where large volumes of the aqueous phase must contact the extrac-
tant, and where losses from solubility and/or entrainment would
be large. However, the solid extractants that are commercially

available tend to lack the versatility and selectivity available
in liquid extractants, and in some cases they suffer problems of
slow absorption and desorption. Most studies to date have dealt
with the relatively few commercially available solid extractants
(4), and applications are limited to a few processes. We shall
address the problem of limited versatility of solid extractants
as well as study the effect of the supporting structure on the
functional group, by synthesizing new polymeric extractants and
comparing their performances against their corresponding liquid
analogues.

POLYMER-SUPPORTED EXTRACTANTS:BACKGROUND

The concept of using solid specialty extractants, though
seemingly commercially neglected when compared with their liquid
analogues, has some basis in experimental work (5). Iminodi-
acetic acid resins have been synthesized as both phenolics (6)
and as styrenics (7), and such solid extractants have been
commercially available under the tradename Dowex Chelating Resin
A-1 (8). Resin A-1 (structure I) can be prepared by suspension
polymerization and is particularly effective in concentrating
divalent ions (8). A derivative structure (II) has been found
useful in separating transition metals from Group IIA metals
(9). Polymercaptostyrene (III) and a polymeric quinolinol have
also been synthesized (10,11).

$$\text{—}\langle O \rangle\text{—}CH_2N(CH_2COOH)_2 \qquad \text{—}\langle O \rangle\text{—}CH_2NCH_2CH_2N(CH_2COOH)_2 \qquad \text{—}\langle O \rangle\text{—}CH_2SH$$
$$\underset{CH_2COOH}{|}$$
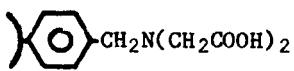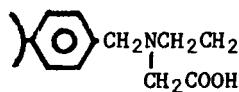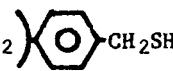
(Polymer; I)   (II)   (III)

Given the early recognition afforded the phosphates and
phosphonic acids as liquid extractants, it is not unexpected that
methods for supporting these systems also received attention. A
polymeric phosphate was prepared by the free radical polymeriza-

tion of diallyl allyl phosphonate (12). The capacity of the
polymer for adsorbing Fe(III) ions from an aqueous $FeCl_3$ solution
was only 0.2 meq/g; this low capacity was probably due to the
high solvation energy of the water because adsorption from
ketones and alcohol solutions raised the capacity to 1-3 meq/g.
The suggestion that polymeric phosphine oxides might prove to be
more effective extractants than the phosphonates based on the
behavior of the homogeneous case (13) has been most recently the
focus of studies by Saegusa and co-workers (14). They synthe-
sized a polymeric phosphine oxide on a polystyrene support and
found that the polymer adsorbed UO_2^{+2} quantitatively from 10^{-6} $\underline{M}$
aqueous solutions.

    Polystyrene-supported phosphonic acids (IV) were synthesized
by the reaction of PCl_3 on chloromethylated polystyrene beads
(15). Phosphorylation occurs both on the aromatic ring and the
chloromethyl moiety giving an acidic resin with a Na^+/H^+ exchange
capacity of 8.0 meq/g. While resin IV displayed no unique selec-
tivity, resins showing enhanced selectivity (16) for divalent
transition metal cations were later synthesized from polystyrene
(resins V, VI).

       (IV)   (V)   (VI)
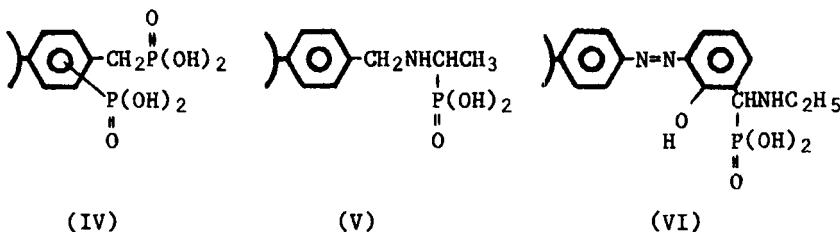
POLYMER-SUPPORTED EXTRACTANTS:PRESENT RESEARCH

    The research (of which this paper is a first report)has as
its goal the examination of solid resin-supported extractants in
comparison with their functionally analogous liquid extractants,

with the hope of defining reagents that combine the flexibility
of liquid systems with the insolubility of polymeric systems.

In carrying out our studies, we need to keep in mind two key
criteria which polymeric reagents must meet in order to be
considered for any industrial process: (1) the polymeric reagent
must be economical and thus readily produced on a large scale
requiring only minimal add-on to current production facilities,
and (2) the polymer must display mechanical stability to usual
pressure drops encountered and chemical stability to strong acids
and bases used in extraction and regeneration. We are recogniz-
ing these criteria by placing our initial emphasis on polystyrene
as the support material. By synthesizing the polystyrene via a
suspension polymerization process, we at once endow the system
with the possibility of maximum physical stability (spherical
beads) with minimum pressure drop problems (≈ 1 mm bead diameter)
utilizing a commercial process (17). Crosslinking the polymer
chains with a difunctional monomer such as divinylbenzene (DVB)
is necessary for mechanical stability. The greater the amount of
crosslinking, the more resistant the bead to mechanical attri-
tion. The tighter, though, that the polymer matrix becomes, the
greater the possible decrease in exchange kinetics, leading to
the choice of a range from 2% to 15% DVB, together with variation
of the macroporosity (17).

Our initial focus is on supporting P=O compounds onto poly-
styrene: phosphinic acids for complexation through ion exchange
and phosphine oxides for complexation through neutral coordina-
tion. With liquid extractants, the combination of various
phosphorus acids and oxides has led to the observation of syner-
gistic extraction (18) where the combined effect of the two is
greater than the sum of the two individual extractants used alone
(19). We have combined phosphinic acid and phosphine oxide
groups onto one polymeric resin; our results, reported below,
give the first indication of synergistic extraction in solid
extractants.

EXPERIMENTAL

Polystyrene Synthesis

Synthesis of the polystyrene support in bead form via
suspension polymerization followed a published procedure (17).
The aqueous phase consisted of gelatin and poly(diallyldimethyl-
ammonium chloride) (Calgon Corp.) as suspension stabilizers while
the organic phase consisted of styrene, variable levels of
divinylbenzene, 1% benzoyl peroxide, and 50% 4-methyl-2-pentanol
as pore-forming agent. The polymerization occurred over a period
of ten hours at 80°C. The alcohol was removed by steam distilla-
tion and the polymer dried in a vacuum oven for twelve hours at
40°C. A -16 +20 mesh cut was used in the subsequent functional-
ization.

Functionalization

Synthesis of the polystyrene-supported phosphinic acid/phos-
phine oxide was achieved by swelling the beads in PCl_3 (Aldrich)
for 2 hours at 25°C followed by the addition of 0.77 mole
anhydrous $AlCl_3$ (Aldrich) per mole copolymer. The mixture was
allowed to stir for 4 hours at 73°C with subsequent hydrolysis in
water.

Characterization

The solids content of the functionalized beads was deter-
mined by draining the wet beads by aspirator for five minutes,
weighing out a ten gram sample, then drying in an oven at 110°C
for 12 hours. The weight ratio, dry to wet, reflects the weight
of solid polymer per gram of wet resin employed.

The cation exchange capacity (CEC) was determined by eluting
the acid form of the resin with 4% $NaNO_3$ and titrating the acid
with NaOH.

The amount of secondary phosphine oxide on the bead was
quantified by iodometric titration (20): the beads were shaken

with an excess of 0.1 $\underline{N}$ I_2 in 2% KI for 16 hours and the iodine
left was titrated with 0.1 $\underline{N}$ $Na_2S_2O_3$.

Zinc Ion Analysis

Each of ten vials contained a given zinc concentration in
five milliliters of solution and 1 meq acid sites on the beads
(0.48 g of the 2% DVB resin). An amount of zinc stock solution
(2 $\underline{N}$ $Zn(NO_3)_2$ in 2 $\underline{N}$ $NaNO_3$) was used to give Zn:acid equivalent
ratios of approximately 0.05, 0.10, 0.20, 0.40, 0.80, 1.00, 1.20,
1.40, 1.60, 1.80; the remainder of the 5 mL solution consisted of
4 $\underline{N}$ $NaNO_3$. Each vial thus contained 4 $\underline{N}$ nitrate ion to give a
high, approximately constant ionic strength (4.0 to 4.3 $\underline{M}$). Each
5 mL solution contained 0.025 microcuries [65]Zn initially, and the
solutions were counted again after overnight equilibration with
the beads. The pH of each solution was measured by a Brinkmann
pH meter.

Copper (II) Ion Analysis

Each of six vials contained a given copper concentration in
ten milliliters of solution and 1 meq acid sites on the beads.
An amount of copper solution (0.3 $\underline{N}$ $Cu(NO_3)_2$) was used to give
Cu:acid equivalent ratios of 0.10, 0.15, 0.30, 0.50, 1.00, 1.50;
the remainder of the 10 mL solution consisted of either distilled
water or 0.01 $\underline{N}$ HNO_3. No attempt was made to maintain a constant
ionic strength in each solution (0.015 to 0.23 $\underline{M}$). After over-
night equilibration, copper ion concentrations were established
by atomic absorption analysis using a Varian AA-1475 series
atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The use of phosphinic acids in solvent extraction studies is
well documented (21,22). Though less acidic than comparable
phosphoric acids, they display a larger uranium extraction

coefficient (18) and can be expected to be more hydrolytically
stable. We decided to study the synthesis and application of
polystyrene-substituted phosphinic acids; the synthesis of
styrenic phosphonic acids has been described (23). The
phosphinic acids form the polymeric analogues of our work on
liquid phosphinic acids (24). The synthesis proceeds through a
phosphinyl dichloride intermediate utilizing a Friedel-Crafts
catalyst. Friedel-Crafts reactions are employed in the synthesis
of chloromethylated polystyrene precursors to anion exchange
resins (25); it is known that this reaction results in not only
chloromethylation of the phenyl rings but also in the formation
of methylene bridges between the phenyl rings to yield what has
been termed secondary crosslinking (26). Given this precedent,
we anticipated the simultaneous formation of phosphinic
acid/phosphine oxide moieties onto the polystyrene support via
the following reaction:
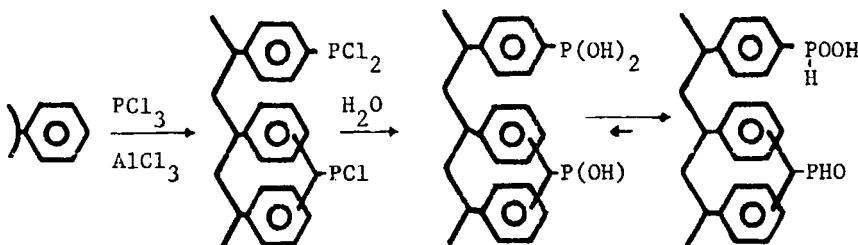
The tautomeric equilibrium has been found to lie well to the
right by Williams and Hamilton (27). It is thus reasonable to
expect simultaneous metal ion exchange and coordination from the
polymeric extractant with a synergistic interaction under favor-
able circumstances (18). A substantiation of this hypothesis was
sought by wet chemical techniques and a metal ion extraction
study; spectroscopic techniques are currently being evaluated.

     The functionalized support is predicted to have two distinct
types of hydrogens not bonded to a carbon atom: an acidic H
attached to the oxygen and a non-acidic H attached to the

phosphorus. The acidic H was determined by ion exchange with Na^+ and subsequent titration with 0.1 $\underline{N}$ NaOH to give the cation exchange capacity (CEC). The non-acidic H was determined by replacement with the iodide ion and back-titration of excess I_3^- with sodium thiosulfate (20) to give a total capacity from which phosphine oxide capacity (POC) was calculated by difference. Non-interference from the acidic H was established by control experiments with pure di(n-octyl)phosphinic acid. Our results are summarized in Table 1. The capacities indicate that the support with the least extent of initial crosslinking (2% DVB) results in a resin with the highest monosubstitution and least phosphine oxide bridging, due primarily to the concomitant loss in entropy upon bridging. As the matrix becomes tighter (5% to 15% DVB), entropy loss becomes less important, and the extent of bridging monotonically increases at the expense of strong acid capacity.

The CEC:POC ratio is expected to impact the metal ion chelating properties of the resin. Results obtained to date are presented in Table 2 and focus on the 2% DVB resin with its corresponding 1:1 acid/oxide molar ratio.

TABLE 1

Resin Capacity as a Function of DVB Content

Resin % DVB	CEC[a] (meq/g)	POC[b] (meq/g)	Total Capacity (meq/g)	CEC:POC Ratio	Solids[c] Content (%)
2	2.00	2.27	4.38	1:1	26.5
5	1.82	3.03	4.85	3:5	29.1
10	1.41	3.26	4.67	3:7	32.2
15	1.18	3.54	4.72	1:3	31.8

[a]Cation exchange capacity

[b]Phosphine oxide capacity

[c]Weight ratio (dry/wet) x 100

TABLE 2.

Metal Ion Extraction by Functionalized 2% DVB Resin

	Vial Number									
	1	2	3	4	5	6	7	8	9	10
Experiment A:										
R_i(Zn)	0.05	0.10	0.20	0.40	.80	1.0	1.2	1.4	1.6	1.8
(meq Zn)$_{resin}$	0.0353	0.0669	0.126	0.231	0.406	0.485	0.561	0.641	0.681	0.733
(meq Zn)$_{soln}$	0.0147	0.0331	0.0735	0.169	0.394	0.515	0.639	0.759	0.919	1.067
solution pH	0.99	0.95	0.91	0.87	0.79	0.77	0.72	0.68	0.65	0.66
% Zn absorbed	70.6	66.8	63.1	57.7	50.7	48.3	46.6	45.6	42.4	40.5
% Resin loaded	3.5	6.7	12.6	23.1	40.6	48.5	56.1	64.1	68.1	73.3
D_{Zn}	25.0	21.0	17.8	14.2	10.7	9.81	9.14	8.78	7.71	7.15
Experiment B:										
R_i(Cu)[a]		0.10	0.15	0.30	0.50	1.0	1.5			
(meq Cu)$_{resin}$		0.0995	0.1483	0.2808	0.4220	0.5300	0.5300			

$(meq\ Cu)_{soln}$	0.0005	0.0017	0.0192	0.0780	0.4700	0.9700
solution pH	1.98	1.75	1.55	1.40	1.33	1.30
% Cu absorbed	99.5	98.8	93.6	84.4	53.0	
% Resin loaded	9.95	14.8	28.1	42.2	63.0	53.0
D_{Cu}	4145	1810	304	112	23.3	11.4

Experiment C:

$R_1(Cu)^b$	0.14	0.30	0.50	1.0	1.5
$(meq\ Cu)_{resin}$	0.1331	0.2640	0.3650	0.5130	0.5550
$(meq\ Cu)_{soln}$	0.0069	0.0360	0.1350	0.4870	0.9450
solution pH	1.60	1.45	1.35	1.20	1.15
% Cu absorbed	95.1	88.0	73.0	51.3	
% Resin loaded	13.3	26.4	36.5	51.3	55.5
D_{Cu}	401	153	56.2	21.8	12.2

[a] $Cu(NO_3)_2$ solution made up with distilled water
[b] $Cu(NO_3)_2$ solution made up with 0.01 N HNO_3

The zinc extraction studies were carried out over a range of
initial ratio values, R_i, where

R_i =(meq M^{2+} initially in solution)/(meq acid sites in the resin).

R_i was varied from 0.05 to 1.8. A constant level of 1 meq acid
sites was utilized against a variable level of $Zn(NO_3)_2$ in 4 $\underline{N}$
$NaNO_3$ with 5 mL total volume of solution; a constant background
of 4 $\underline{N}$ nitrate ion was thus present, independent of the zinc
content, allowing for nearly constant ionic strength. The extent
of zinc extraction by the resin was followed by the decrease in
aqueous phase ^{65}Zn activity from an initial level of 0.025 micro-
curies per 5 mL. The equilibrium pH of each solution was also
recorded. A control run consisting of 0.50 g unfunctionalized
polystyrene and an initial concentration of 1.0 meq Zn^{2+} was
found to remain at 1.0 meq Zn^{2+} in solution regardless of the
equilibration time. The % M^{2+} absorbed onto the resin and
remaining in solution and a modified distribution coefficient,
$D_{M^{2+}} = $ meq $M^{2+} \cdot g^{-1}$ resin/meq $M^{2+} \cdot mL^{-1}$ sol., is reported in
Table 2. In order to determine the validity of using this ratio
as the distribution coefficient, the relationship of log
$[M]_{resin}$ to log $[M]_{aq}$ was examined. A linear regression
analysis of log[(meq Zn)$_{beads}$/g beads] $\underline{vs}$ (log[(meq
Zn)$_{soln}$/mL soln] + 2 pH) for loadings up to 1:1 yields a line
with slope 1.02, which indicates that the same extent of zinc
aggregation (probably monomeric) occurs in both the resin and
solution.

The zinc data indicate that there was 70% extraction of Zn^{2+}
at low initial zinc, decreasing to 48% at an initial equivalent
ratio, while the loading increased as excess Zn^{2+} was added to
the system to 73% loading at the highest ratio tested. While we
have not found previous work on styrenic phosphinic acids, there
has been a cation exchange study on styrenic phosphonic acids
which is comparable to ours: Bogoczek and Surowiec (28) found

that their macroporous resin extracted 22% of the Zn^{2+} at a solution pH of 5.59 and a zinc to total available resin acid ratio (R_i) of 0.5. We can compare this with a value interpolated from Table 2 of 56% extraction at pH 0.85. At pH 5.59 extraction in our experiment should have been 100%, since the distribution coefficient for Zn would be 10^4 higher at that pH.

Data from the Cu(II) study was handled in a similar manner. The R_i values ranged from 0.10 to 1.5. The difference in the two copper runs is the nature of the solutions: the copper nitrate was dissolved in pure water in the first case (ionic strength 0.015 to 0.23 $\underline{M}$) and in 0.01 $\underline{N}$ HNO_3 in the second case (ionic strength 0.02 to 0.23 $\underline{M}$). The results show a very high level of extraction for R_i values up to 0.5. At a 1:1 initial ratio, the resin absorbed $\approx$50% of the metal ion in solution for copper, as it did for zinc. The exchange constant, K_{ex}, for copper, shown in the equation below,

$$\frac{1}{2}(Cu^{+2})_{aq} + (HR)_{resin} \rightleftarrows \frac{1}{2}(CuR_2)_{resin} + (H^+)_{aq}$$
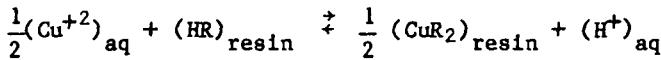
$$K_{ex} = [(CuR_2)_{resin}]^{\frac{1}{2}}[(H^+)_{aq}]/[(Cu^{+2})_{aq}]^{\frac{1}{2}}[(HR)_{resin}]$$

is calculated to be 0.34 ± 0.01 for the first case and 0.28 ± 0.01 for the second case. In reference 28 the phosphonic acid resin was reported to extract 25% of the Cu^{2+} at a solution pH of 4.86 and a copper to total available resin acid ratio of 0.4. Again, our interpolated values of 89% extraction at pH 1.5 and 81% at pH 1.4 indicate a much greater extracting capability for the phosphinic acid/phosphine oxide bifunctional resin.

CONCLUSION

The high affinity of our resin for the metal ions tested is evidence suggesting a cooperative interaction between the phosphinic acid and phosphine oxide moieties which may be

synergistic. It is reasonable to suspect that the phosphine oxide groups are increasing the extent of metal ion extraction by replacing the water in the metal coordination sphere (29). We will be publishing a thorough account of our metal ion extraction studies shortly (30).

Experiments currently in progress aim to test the hypothesis of polymer-supported synergistic extraction. Phosphorus nmr studies will provide spectroscopic evidence for the existence of two distinct phosphorus groups within the bead. We have also synthesized a polymeric extractant which is almost pure phosphine oxide in order to determine the importance of the phosphinic acid groups and will be reporting its extracting capabilities in due course.

ACKNOWLEDGMENTS

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