DOE/ER/13591--6

DE93 001835

POLYMER-BASED SEPARATIONS:
SYNTHESIS AND APPLICATION OF POLYMERS FOR IONIC AND MOLECULAR RECOGNITION

Triennial Performance Report
August 1, 1989 - July 31, 1992

Spiro D. Alexandratos

University of Tennessee
Knoxville, Tennessee 37996

Received by OSTI

OCT 21 1992

January 1992

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG05-86ER13591

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

I. INTRODUCTION

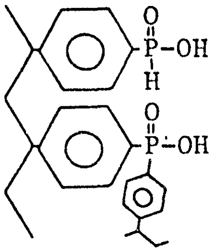
The application of separations science to many areas of research is of continuing importance.[*] The recovery of strategic metals from low grade ores, heavy metal ions from plutonium processing facilities (as noted by a July 1991 conference at the Battelle Pacific Northwest Laboratories), and toxic metal ions (such as chromium) from groundwater are only a few of the areas confronting metal ion separations research. Molecular separations are also gaining increased emphasis with the need to recover commodity chemicals from microbial fermentation processes in an energy-efficient manner, as well as medicinals produced through recombinant DNA techniques, and toxic organic substances (such as PCBs and hydrocarbons) from water in the environment.

Polymer-based separations have utilized commercially available resins such as the sulfonic, acrylic, and iminodiacetic acid resins and the XAD series (from Rohm & Haas). Modification reactions on polymer supports such as polystyrene have led to important insights by the covalent bonding of a single type of ligand on a support and determining the metal ion affinities which result.[1]

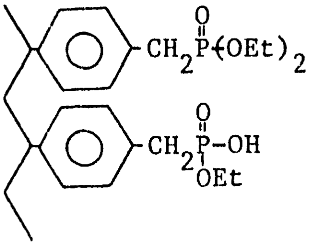
---

[*] A complete set of references may be found in the accompanying Renewal Proposal. Only references to our research carried out during the current period (1989-1992) will be given in this Report.

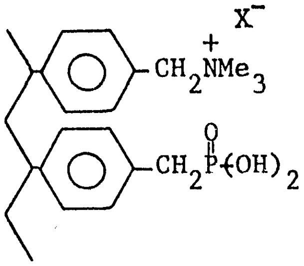
Our approach to the design of selective polymeric reagents for reaction with a targeted metal ion has been the synthesis of polymers with two different types of covalently bound functional groups, each operating on the ions through a different mechanism.[2] These **dual mechanism bifunctional polymers** (DMBPs) operate through an access mechanism (which can be relatively aspecific in attracting ions into the polymer matrix) and a recognition mechanism (which reacts with the targeted ion and is responsible for the polymeric reagent's observed specificity). There are three classes of DMBPs, each defined by the recognition mechanism; the access mechanism for each class is ion exchange due to that ligands' hydrophilicity and compatibility with metal ions. The Class I ion exchange/redox DMBPs operate through a reduction of certain metal ions to the pure metal. The Class II ion exchange/coordination DMBPs selectively complex certain metal ions. The Class III ion exchange/precipitation DMBPs react with targeted metal ions to produce insoluble metal salts. An example from each class is indicated below.



Class I



Class II



Class III

Research during the current period dealing with metal ion recognition has focused on the Class I and II DMBPs.

The mechanisms by which the phosphinic acid ion exchange/redox resins operate has been extensively studied. A set of conditions have also been defined wherein the phosphonate monoester/diester ligands in an ion exchange/coordination resin cooperate synergistically in certain cases to complex far higher levels of metal ions than either one could alone.

Another area of research which will be summarized in this Report is the design of a new set of ion-selective polymers in which the ligands are immobilized by interpenetrating polymer network formation. The design of polymeric reagents which display molecular recognition for neutral substrates will also be introduced.

II. POLYMER-BASED SEPARATIONS:
METAL ION RECOGNITION BY COVALENTLY-BOUND LIGANDS

The metal ion specificity of the phosphinic acid resin is best seen by a comparative study with the sulfonic acid resin.[3] Both resins were contacted with dilute (10^{-4}N) solutions of Fe(III), Hg(II), and Mn(II) as the nitrate salts in varying concentrations of HNO_3 (4N, 2N, 1N, 0.2N, 0.1N, 10^{-2}N, 10^{-3}N, and 10^{-4}N) in one set; in a second set, $NaNO_3$ was added to each of the previous solutions to keep the total nitrate concentration at 4N. At equilibrium, the distribution coefficient (D) of each ion was determined radiometrically and correlated (as its logarithm) with the final pH of the solution. The points given in Table I are representative of the entire set.

Table I. Comparison of the Sulfonic with the Phosphinic Acid Resin for Fe(III), Hg(II) and Mn(II) Complexation

	Sulfonic Acid			Phosphinic Acid		
pH_f	-0.60	0.00	0.70	-0.60	0.00	0.70
	with $NaNO_3$ added					
logD (Fe)	0.91	0.86	1.07	3.76	3.89	4.41
logD (Hg)	0.61	0.73	0.91	3.32	3.86	3.78
logD (Mn)	0.69	0.63	0.69	0.42	0.75	1.44
	without $NaNO_3$ added					
logD (Fe)	0.96	2.54	4.12	3.71	4.20	4.51
logD (Hg)	0.59	2.13	2.72	3.56	3.69	3.61
logD (Mn)	0.69	1.66	3.05	0.36	0.67	1.74

A number of conclusions can be made from this study:

(i) the complexing ability of the phosphinic resin is not affected by the presence of a large excess of sodium ions;

(ii) the sulfonic resin suffers a dramatic loss in its ability to complex heavy metal ions in the presence of Na^+ due to the non-selective nature of its ion exchange;

(iii) the phosphinic resin complexes higher levels of Fe and Hg ions than the sulfonic resin in solutions of 1N acid or greater due to the strongly coordinating phosphoryl oxygen; the optimum operating pH is lower for the sulfonic than the phosphinic resin when complexation occurs by ion exchange;[4]

(iv) Mn(II) is complexed to a lesser extent under these conditions by the phosphinic resin since, as a hard ion, its complexation is not favored by the soft phosphoryl oxygen; Fe(III) is complexed to a great extent, even though it is a hard ion, perhaps because of an entropy-driven coordination where release of the waters of hydration around the trivalent salt provides the favorable free energy of reaction; complexation of the soft Hg(II) ion is enthalpy-driven, and remains constant over a range of conditions (vide infra) due to the reduction mechanism.

The phosphinic resin reduces the mercuric ion to mercury metal at concentrations greater than 10^{-5}N, even in the presence of a large excess of sodium ions.[5] Metal ion reduction also obviates any loading effect on the resin due to the absence of ions within the resin at equilibrium:
the amount sorbed from a concentrated solution is almost the same as from a dilute solution since there are no unfavorable electrostatic interactions among complexed sites. Thus, the logD value when the phosphinic resin contacts a 0.2N Hg(II) solution at pH 2 is 3.88, compared to 3.80 when that solution is 10^{-4}N. With Fe(III), where no reduction occurs, the logD value from a 0.2N solution is 0.40, compared to 4.94 from a 10^{-4}N solution.[6]

Silver ions are reduced to silver metal by the phosphinic resin, but only at relatively high ionic concentrations coupled with low acid solutions. This difference in Hg(II) vs. Ag(I) reduceability was confirmed in a study of the reduction kinetics at different temperatures and solution pH values.[7] The solutions contained 1 milliequivalent (mequiv) of metal ion per mequiv of phosphorus ligands on the resin. At each of several contact times (0.25, 0.50, 1, 3, 5, 8, 12, 17 and 24 hours), the total percent metal complexed from solution was determined titrimetrically, as was the amount reduced and that which remained ionic within the resin. The sorption of Hg from solution occurs at a faster rate compared to Ag: with a 2% divinylbenzene (DVB) crosslinked gel resin, >90% of the Hg is sorbed within 3 h compared to 72% of the Ag. Hg sorption is quantitative between 5 and 8h while Ag is only 82% sorbed at 24h. The redox components for both Hg and Ag are identical up to 1h. The higher sorption level for Hg is reflected in a higher ionic component relative to Ag; Hg reduction exceeds that of Ag after 1h. At equilibrium, almost all of the metal (Hg and Ag) which has been sorbed is reduced. A macroporous resin yields the same results as the gel with Ag and quantitative Hg sorption within 15 minutes (compared to 5-8h with the gel).

This study suggests that Ag kinetics are due to a slow reaction which controls the overall rate of diffusion while Hg kinetics are diffusion-limited due to a fast reaction rate. The faster rate of Hg reduction is consistent with the stoichiometric requirements of the reaction: Hg(II) reacts with the P-H bond in a 1:1 molar ratio whereas Ag(I) reacts in a 2:1 ratio. If the mechanism is one in which two silver ions must be close enough to each other and to a single P-H bond for the electron transfer to occur, then the rate of this reaction may be inherently slower than reaction between a single metal ion and a single P-H bond.

A comparative study of the Class II DMBPs with a series of metal ions from $HNO_3/NaNO_3$ solutions (4N/-, 2N/2N, 1N/3N, and 0.2N/3.8N) was carried out.[8] The sulfonic and phosphinic acid resins were also included. Two important conclusions about the ion exchange/coordination resins arose from this study.

The bifunctional phosphonate monoester/diester resin displays a unique mechanism of complexation with Ag(I), for which it has the greatest affinity of any resin synthesized in this study. The bifunctional resin coordinates far more silver ions than expected from the performance of the two monofunctional resins. In contrast to this, the monoester resin outperforms both the bifunctional and diester resins for Hg(II) and Fe(III). Table II gives the results from 4N HNO_3.

Table II. Distribution Coefficients for Fe, Hg and Ag Nitrates with Monoester/Diester, Monoester, and Diester Resins from 4N HNO_3 Solution

	D(Ag)	D(Hg)	D(Fe)
Monoester/Diester	2924	15	309
Monoester	439	23	3802
Diester	463	3	1

The phenomenon wherein two ligands on a bifunctional polymer cooperate to complex more of the target species than either one could alone is termed **supported ligand synergistic interaction.** Synergism between soluble, low molecular weight metal ion complexing agents has been observed; it is now extended to polymeric reagents.

The purely coordinating dialkyl phosphonate ester resins display selectivities that are quite different from phosphorus acid resins. The bulkiness of the dialkyl groups can be used to control the metal ion selectivity: the dibutyl ester resin is better able to distinguish ions in the series Ag>Hg>Fe than is the dimethyl ester resin; this may reflect a size-selectivity for the mononitrate vs. the dinitrate and trinitrate salts (the background solutions are as noted above and the ions must be fully nitrated). Size alone is not determining since $Zn(NO_3)_2$ and $Mn(NO_3)_2$ are complexed to a very slight extent relative to $Hg(NO_3)_2$ indicating that the polarizability of the central metal ion is still an important variable. This is probably the variable which is responsible for the monoester resin's ability to complex silver and gold anions from alkaline solutions.[9]

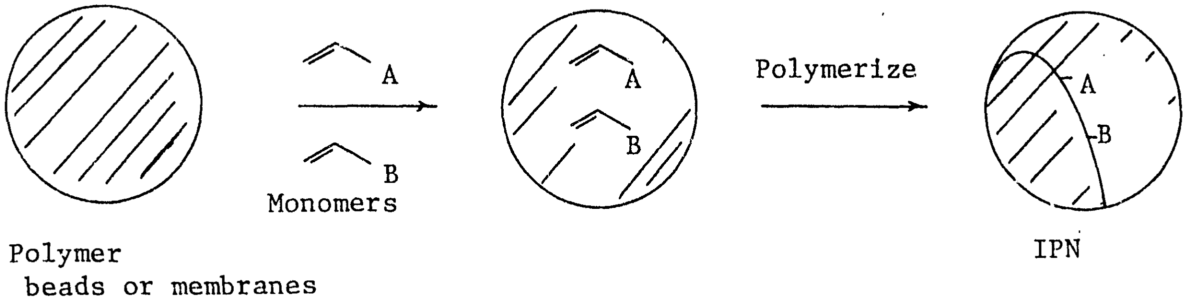
III. POLYMER-BASED SEPARATIONS:

METAL ION RECOGNITION BY IPN-IMMOBILIZED LIGANDS

The modification of polymer supports with ligands which can display significant ionic recognition has centered upon chemistry which covalently bonds the ligands to the support.

This has been the preferred method of immobilization because of the polymeric reagents' long-term stability. Given our focus on bifunctional polymers, however, the choice of reactions which lead to two types of ligands in a known ratio on a support, without any side reactions, is limited. Additionally, the covalent immobilization of well-defined ligands on readily available membranes such as polypropylene is not a straightforward process.

A convenient method has been developed during the current research period which immobilizes ligands through the formation of interpenetrating polymer networks (IPNs). The final product displays excellent long-term stability and is applicable to both beads and membranes.[10] The concept is illustrated in equation 1. A support (e.g., polystyrene beads or polypropylene membranes) is contacted with a solution containing one or more monomers. After a certain time, the monomers are polymerized within the support to form an IPN. A crosslinking agent, such as DVB, in the monomer solution causes the IPN to be immobilized with a stability which seems to be permanent.[11] Well-defined polymeric reagents can thus be synthesized in a form directly applicable to separations.



(1)

This concept has been applied to the synthesis of ion exchange/coordination DMBPs.[12] Polystyrene beads are contacted with a solution of two monomers, one of which will be responsible for ion exchange and one which has a specific complexing affinity for a targeted metal ion; DVB in the solution gives the final IPN its long-term stability. In an initial study, the IPN was constructed with a carboxylic acid group (for ion exchange) and an imidazole group (for its ability, observed in enzymes, to complex certain transition metal ions). The bifunctional IPN was thus synthesized from the copolymerization of ethyl acrylate and N-vinylimidazole.[13] Hydrolysis of the acrylate led to the carboxylic acid group (the polymerization with acrylate was more reproducible than that with acrylic acid). The monofunctional IPNs from N-vinylimidazole and ethyl acrylate were prepared as controls; their final capacities were 4.38 and 5.32 mequiv/g, respectively (the latter after hydrolysis). The bifunctional IPN had an acid capacity of 2.55 mequiv/g and a base capacity of 3.33 mequiv/g. All values, determined titrimetrically, were in agreement with those calculated from monomer uptake weights.

A new, thermodynamically rigorous, method was developed to quantify metal ion affinities by the bifunctional polymeric reagents. This method involves the calculation of **binding constants.** In this technique, a Langmuir isotherm is first determined between the polymer and the metal ion; the isotherm is then transformed into a y-reciprocal plot from which the binding constant is calculated as the ratio of the slope to the intercept (equation 2).

$$c/r = (1/S_t)c + 1/(KS_t) \qquad (2)$$

c = mequiv substrate per mL solution at equilibrium

r = mequiv substrate per gram polymer at equilibrium

S_t= saturation capacity (mequiv/g polymer)

K = binding constant

Points for the y-reciprocal plot are taken from the (r vs.c) adsorption isotherm within 20-80% of saturation. A portion of both plots for the Cu(II) interaction with the imidazole, acid/imidazole, and acid IPNs after a 24 h contact time are shown in Figure 1. The binding constants are 617, 252, and 51 M^{-1} for the three IPNs, respectively. The saturation

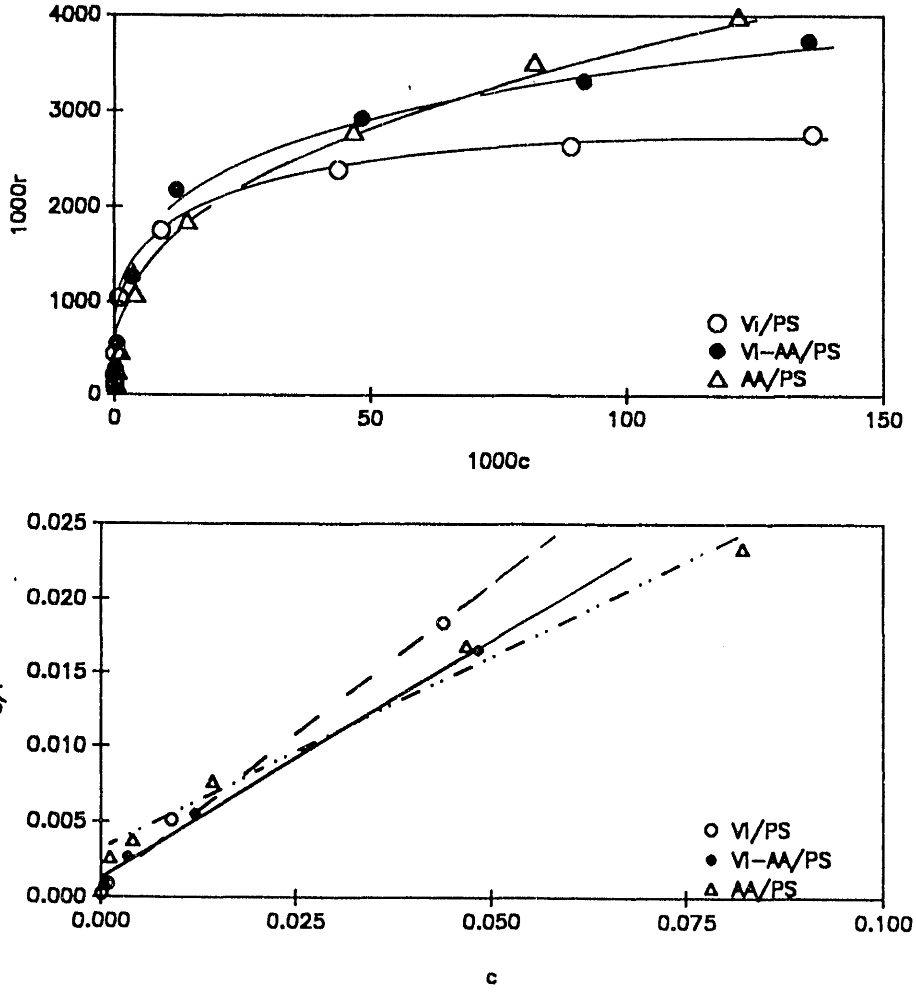


Figure 1. Adsorption isotherm and y-reciprocal plots for Cu(II) binding with imidazole (VI), VI/acid, and acid (AA) IPNs.

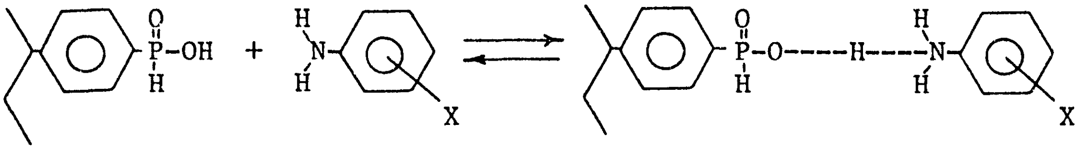
capacities increase in the order 2.8, 3.3, and 4.6 mequiv/g, respectively. The binding constants for Co(II) are 99, 76, and 19 M^{-1}, respectively, with saturation capacities all at 2.9 mequiv/g. The results indicate that IPN formation does not hinder metal ion complexation, that the inherent selectivity of imidazole for Cu(II) over Co(II) is maintained within the IPN, and that the bifunctional network offers a different binding environment to the metal ion relative to the monofunctional networks. Studies with monomer pairs which lead to IPNs wherein the ligand interactions enhance the extent of metal ion complexation are in progress.

IV. POLYMER-BASED SEPARATIONS:

MOLECULAR RECOGNITION BY POLYMER-SUPPORTED REAGENTS

Given the importance of molecular separations, research was begun during the current period in defining the parameters in polymer-supported reagents which determine ligand-substrate selectivity.

Biomolecules, medicinals, amino acids, and commodity chemicals are the substrates of interest in molecular separation processes. The approach taken in this phase of our research was to quantify the interactions of a given functional group with a ligand covalently bound to a polymer support, as the electron density at that functional group was varied.[14] This was accomplished with substrates such as anilines, benzoic acids and phenols by varying the substituents on the aromatic ring. Thus, for example, the polymer-supported phosphinic acid's interaction with the $-NH_2$ functional group was monitored with a series of anilines (equation 3). The substituents chosen, in order of



(3)

increasing electron withdrawing strength, are pCH_3O, pCH_3, mCH_3, H, mCH_3O, pCl, and mCl. The amount complexed of each substrate can then be correlated to the electron density at the functional group by the Hammett substituent sigma constants (-0.28, -0.14, -0.06, 0, 0.10, 0.24, and 0.37, for the substituents as given above).

It was found that moderate interaction energies are important to ligand-molecule selectivity. If an interaction is very strong or weak, then small differences in electron density at the functional group will not be able to induce selectivity. An interaction of moderate strength can allow the ligand to distinguish among small differences at the functional group. This is illustrated by the interaction of the sulfonic, phosphinic and carboxylic acid ligands with the substituted anilines (Figure 2).[15] Both the strongly interacting sulfonic and weakly interacting carboxylic acids are non-selective toward the $-NH_2$ group. Only the phosphinic acid ligand is selective enough to distinguish electron density differences at the functional group. This selecti-

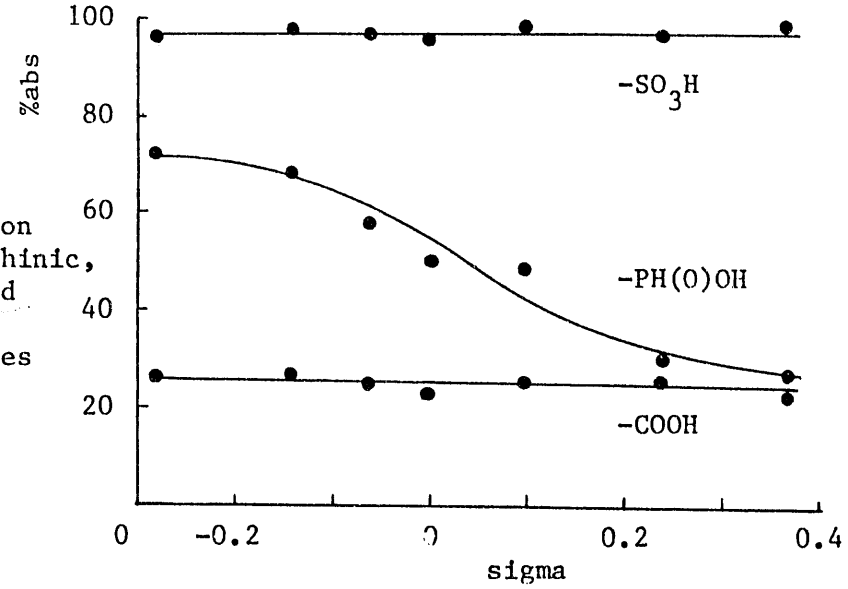


Figure 2. Interaction of sulfonic, phosphinic, and carboxylic acid ligands with substituted anilines (%absorbed vs. substituent sigma constant)

vity may be a function of pK_a/pK_b differences between the ligand and substrate.

The principal focus in the design of selective polymeric reagents has been on the ligand-substrate interaction. We have recently found, however, that the polymer support itself, far from being an inert matrix on which ligands are to be immobilized, plays a critical role in the extent of selectivity. This was first observed in the complexation of substituted benzoic acids by the dimethylamine ligand covalently bound to polystyrene. As the polymer's rigidity increases (by increasing the amount of DVB from 2 to 25%), the ligand becomes more selective in its complexation of the different benzoic acids.[16] This is illustrated by the percent complexed from 0.01M solutions of the least acidic (p-anisic acid) and most acidic (m-chlorobenzoic acid) substrates: the 2% DVB polymeric amine complexes 71% and 84% of the two substrates, while the 25% DVB amine complexes 24% and 70% of the substrates. The other acids, with substituents as indicated above, are at intermediate values.

The concept that the polymer surrounding a ligand can influence its interaction with a substrate has been termed the **microenvironmental effect** in order to emphasize that a ligand on a polymer does not necessarily behave as it would if it were dissolved in solution. A systematic procedure has been proposed which quantifies matrix effects on the ligand's microenvironment:[17] (1) synthesize polymeric reagents with a given ligand bonded onto different matrices; (2) choose a series of aromatic substrates with a common functional group and vary the electron density at that group with different substituents on the aromatic ring; (3) calculate binding constants from the Langmuir isotherm of each substrate: a comparison of binding constants across different matrices quantifies the effect of the microenvironment on each ligand-substrate interaction; (4) correlate the binding constants with the Hammett sigma constants: with a given matrix, the slope is a measure of the interaction's sensitivity to electron density changes and a comparison of slopes across different matrices provides a measure of how the polymeric microenvironment influences that sensitivity.

The microenvironmental effect for the dimethylamine - benzoic acid interaction is quantified by noting that the binding constant for the 2% DVB resin with p-toluic acid is $32.13M^{-1}$ and for m-chlorobenzoic acid is $126.19M^{-1}$, while the 15% DVB resin has binding constants of $15.39M^{-1}$ and $67.99M^{-1}$ for the two substrates, respectively. Correlating the binding constants for all of the substrates with their substituent constants shows that the 15% DVB resin is 12% more sensitive to electron density changes relative to the more flexible 2% DVB matrix. Weaker substrate binding with increasing matrix rigidity may be due to steric effects within the matrix: at higher crosslink levels, the polymer chains lose their ability to adopt new conformations as proximate ligands bind substrates and this could result in longer ligand-substrate distances (hence lower binding constants) in order to minimize steric crowding. Continuing studies along these lines are given in the accompanying Renewal Proposal.

REFERENCES: Publications 1989-1992

1. S.D. Alexandratos

   Polymer-Supported Reagents with Enhanced Ionic Recognition

   Separation and Purification Methods 1992, in press.

2. S.D. Alexandratos, D.W. Crick, D.R.Quillen and C.E.Grady

   Polymeric Ligands for Ionic and Molecular Separations

   Am. Chem. Soc. Symposium Series 1992, in press.

3. S.D. Alexandratos and D.R. Quillen

   Comparison of Phosphinic Acid with Sulfonic Acid Resins

   Solvent Extraction & Ion Exchange 1989, 7, 511.

4. G.K. Schweitzer, A.M.B.M. Radzi and S.D. Alexandratos

   Cation Affinity Series for Carboxylic, Phosphinic and Sulfonic Acid Ion Exchange Resins

   Analytica Chimica Acta 1989, 225, 323.

5. S.D. Alexandratos and D.R. Quillen

   Targeted Metal Ion Complexation by Reactive Polymers

   Reactive Polymers 1990, 13, 255.

6. S.D. Alexandratos and D.R. Quillen

   Metal Ion Loading Capacities of Reactive Polymers with Specific Recognition Mechanisms

   Solvent Extraction & Ion Exchange 1989, 7, 1103.

7. S.D. Alexandratos and P.T. Kaiser
Reaction Kinetics of Polystyrene-Based Phosphinic Acid
Ion Exchange/Redox Resins with Metal Ions
Solvent Extraction & Ion Exchange 1992, in press.

8. S.D. Alexandratos, D.W. Crick and D.R. Quillen
Development of Bifunctional Polymers for Ionic Separations
Industrial & Engineering Chemistry Research 1991, 30, 772.

9. J.D. Miller and S.D. Alexandratos
Composition for Extracting Gold and Silver Anions from
Alkaline Solutions and Processes for Making Same
United States Patent 4,894,407 (Jan. 16, 1990)

10. S.D. Alexandratos, M.A. Strand and C.M. Callahan
Interpenetrating Polymer Networks as Highly Stable
Metal Ion Separation Agents
Advances in Interpenetrating Polymer Networks,
D. Klempner and K.C. Frisch, eds.; 1990, vol.2, pp.73-99.

11. S.D. Alexandratos, P.R. Danesi and E.P. Horwitz
Interpenetrating Polymer Network Ion Exchange Membranes
United States Patent 4,879,316 (Nov. 7, 1989)

12. S.D. Alexandratos, C.E. Grady and D.W. Crick
Bifunctional Interpenetrating Polymer Networks
Am.Chem.Soc., Advances in Chemistry Series 1992, in press.

13. S.D. Alexandratos, C.E. Grady and D.W. Crick
Synthesis of Bifunctional Interpenetrating Polymer Networks as Ion-Complexing Agents
Macromolecules 1991, 24, 6365.

14. S.D. Alexandratos and P.T. Kaiser
Molecular Recognition by Polymer-Supported Reagents Defined through Linear Free Energy Relationship Studies
Industrial & Engineering Chemistry Research 1990, 29, 1306

15. S.D. Alexandratos and P.T. Kaiser
Polymer-Supported Reagents for Molecular Separations
Solvent Extraction & Ion Exchange 1989, 7, 909.

16. S.D. Alexandratos, P.T. Kaiser and C.E. Grady
Network Structure as a Variable in Molecular Recognition
Solvent Extraction & Ion Exchange 1991, 9, 309.

17. S.D. Alexandratos, C.E. Grady, P. Merda and P.T. Kaiser
Binding Constants as a Probe of the Microenvironment in Polymer-Supported Reagents
Journal of the American Chemical Society 1992, in press.

END

DATE
FILMED

12/22/92