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METAL ION COMPLEXATION USING SOLVENT IMPREGNATED RESINS AND BIFUNCTIONAL INTERPENETRATING POLYMER NETWORKS

A Thesis

Presented for the

Master of Science

Degree

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Anne Amanda Kriger

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DEDICATION

This work is dedicated to my husband, Scott, who has given me encouragement, love and support, and to my parents, Henry Tyson Hood and Betty Wayne Hood, who have always believed in me.

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ABSTRACT

Solvent impregnated resins (SIRs) and bifunctional interpenetrating polymer networks (IPNs) are described in this work, and evaluated for metal-ion recovery. Special attention is directed toward identification of synergistic extraction systems. Preparative schemes for SIRs are discussed, including both wet and dry impregnation methods. The presence of synergism is determined by comparing metal-ion distributions in bifunctional systems, with distributions obtained by contacting the metal-ion solution with each of the functionalities individually.

SIRs prepared using a carboxylic acid resin impregnated with liquid extractants (di-n-hexylsulfide, 3,6-di-thiaoctane) showed positive results suggesting synergistic extraction of Hg^{2+} at pH 6.0 in 0.10 N acetic acid. A diethylester resin impregnated with Cyanex 272 also exhibited synergistic extraction of europium(III), at pH 2.0.

A bifunctional vinylpyridine/acrylic acid IPN synergistically complexed several first-row transition metal-ions, including Zn^{2+}, Ni^{2+}, and Co^{2+}, at pH 6.0 from a 0.6-N acetic acid matrix. Cu^{2+} and Hg^{2+} were also readily extracted, however, both the vinylpyridine and the acrylic acid ligands extracted the ions equally as well as the bifunctional polymer.

Based on results with selected metal cations, synergistic extraction systems have at least two features in common. First, the ligand which does not ion-exchange, is in the same hard/soft Lewis acid/base category as the metal ion of interest. For example, a ligand such as di-n-hexylsulfide, which binds

through sulfur, could be expected to complex with Hg^{2+}, a very soft Lewis acid. Second, the operative pH is one at which the metal ion is likely to occur as a cation, rather than a metal hydroxide. These conclusions warrant further investigation, to facilitate the design of bifunctional extraction systems which effectively isolate target metal ions from aqueous media.

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LIST OF ABBREVIATIONS

acrylic acid interpenetrating polymer network (IPN)	AA
bifunctional acrylic acid/vinylpyridine IPN	bif
carboxylic acid resin	$COOH$
distribution coefficient	D
diethylester resin	DE
di-n-hexylsulfide	DHS
3,6-dithiaoctane	DIO
1,1-heptylmethylnonanoic acid	HMHN
2-thenoyltrifluoroacetone	HTTA
interpenetrating polymer network	IPN
mass balance	MB
polystyrene beads	PS
phosphinic acid resin	phos
synergistic coefficient	s. c.
solvent impregnated resin	SIR
sulfonic acid resin	SO_3H
tributylphosphate	TBP
1,4,8,11-tetrathiacyclotetradecane	TT14C4
3,6,10,13-tetrathiapentadecane	TTPD
vinylpyridine IPN	VP

CHAPTER I

GENERAL INTRODUCTION AND OVERVIEW

INTRODUCTION

Polymeric reagents have been used for metal-ion separation, concentration and recovery processes for several decades. The metals targeted in this work include europium, uranium and several first row transition metals because of their important industrial applications, and mercury(II), because of its toxicity.[1-5]

The primary approach to metal-ion recovery used in this work employs solvent impregnated resins (SIRs). SIRs are an attractive approach because unique selectivities are possible by proper selection of the liquid extractant, while maintaining the advantage of complete phase separation associated with polymer extractants. Extraction chromatography, a term used for the application of SIRs, has been widely utilized and is well reviewed by Cerrai and Ghershini.[6] SIR preparation involves swelling polymer beads in an appropriate solvent containing a hydrophobic liquid extraction reagent. The liquid extractant, which is mobile within the polymer matrix, may behave much like it does in a solvent extraction system; which is not a new concept.[7] Application of liquid reagents adsorbed onto solid substrates was done by Tswett, the father of liquid-solid chromatography, who used diatomaceous earths among other things, as a substrate.[8] More recently, typical supports have been polystyrene or functionalized resin beads.[9-12] Both types of resins were used in this work. The functionalized beads impregnated with a liquid

extractant were of primary interest, and polystyrene impregnates were used as a control, to determine the extractive capability of the liquid reagent working alone. Special attention was directed toward identification of the presence or absence of synergism in the bifunctional SIRs. Synergism is a term applied to an enhanced extraction exhibited by certain combinations of ligands, such that the amount of analyte extracted, a metal ion in this case, is greater than that which can be extracted due to the additive effect of the two ligands operating individually. The term synergistic extraction was introduced by Coleman (Oak Ridge National Laboratory)[13], although the phenomenon was reported earlier in the literature.[14,15]

Successful application of SIRs for metal-ion recovery has been reported on a number of levels ranging from the laboratory scale to pilot plant to full-scale work.[16-18] The work in this thesis is laboratory scale, using dilute metal-ion solutions and very small amounts of resin. Equilibrations were carried out in scintillation vials, rather than eluting through packed columns. This permitted sampling and analysis of the metal-ion solutions after contact with the resins.

The primary methods of analysis used in this work were radiochemical techniques and atomic spectroscopy (absorption and emission). Essential to making good measurements and correctly interpreting data is an understanding of how measurements are made, and identification of the limitations of different techniques. A brief discussion of the principles and instrumentation for the above listed techniques is presented later in this chapter.

Radiochemical measurements require conversion of ionizing radiation into a form that can be detected and quantified. This is accomplished using scintillators. A scintillator (also called a fluor) is a solid, liquid or gas which emits very short lived flashes of light when penetrated by ionizing radiation.[19] The scintillator used for gamma spectrometry is almost always a crystal, while liquid scintillators are used in conjunction with alpha and beta particles.[20]

Gamma counting

A NaI(Tl) well-type device was used for gamma assays in this work. The scintillator is a NaI crystal into which a recess or well has been cut. The sample, placed within the well, ensures that a large portion of the emitted radiation is detected because the sample is almost completely surrounded by the crystal. The NaI crystal is mounted in a light-tight container to minimize stray light. The side of the container which faces the sample is very thin so almost all the radiation may penetrate it. A reflective finish is applied to all sides of the scintillator except the end facing the photomultiplier tube (PMT), to permit maximum transfer of the light emitted by the crystal to the photomultiplier. The photocathode emits electrons when bombarded by light. These electrons are accelerated towards a positive electrode by striking metallic elements called dynodes. Secondary electrons are released upon collision with each dynode; thus the number of electrons increases proceeding down the tube. The PMT output is an electrical pulse whose amplitude is proportional to the number of photons striking the photocathode.[21] A more detailed discussion of PMTs has been published by Ingle & Crouch.[22]

Beta counting

Beta (β^-) emitting radionuclides release disintegration energy by the emission of electrons.[23] Since electron pathlengths are short, it is useful to place the sample into a scintillation cocktail to detect the radiation. A scintillation cocktail is a solution consisting of a solvent and a fluor. The beta particles excite the solvent molecules which transfer the energy to the fluor by a collision process. The fluor returns to its ground state by emitting photons. The number of photons produced is proportional to the energy of beta particles.[24] This light is measured using a PMT.

Alpha counting

Experiments using uranium were assayed employing photon-electron-rejecting alpha liquid scintillation spectrometry (PERALS®). This instrument was designed by Mr. Jack McDowell and his associates at Oak Ridge National Laboratory for efficient and accurate counting of alpha-emitting nuclides.[25] As with beta counting, a liquid scintillation solution is used to permit light collection and detection using a PMT. The instrument is capable of rejecting light produced by beta and gamma particles which may also be present in the sample. The basis for rejection is that light pulses produced from alpha particles are delayed on a time scale compared to that of beta- or gamma-produced pulses.[26] Pulse-height discrimination is accomplished by an electronic circuit. A more detailed discussion of the instrumentation has been previously reported.[27]

The uranium sample preparation is slightly more involved than for counting

beta- or gamma-emitting samples. The sample is first extracted into a beta- or gamma-emitting samples. The sample is first extracted into a scintillation cocktail. This cocktail contains an extractant for phase transfer, as well as a fluor and an energy-transfer agent. Following extraction into the scintillator, the sample is sparged with dry, toluene-saturated argon gas, to remove oxygen. The sample is then ready for analysis.

Practical considerations when using scintillation counting include counting efficiency, interferences such as quenching, any other source of radiation which can contribute to background, and phase compatibility of the sample and the cocktail. Environmental radiation and electronic noise are the primary sources of background. The electronic background level due to the instrumentation is minimized by employing two PMTs and a coincidence circuit that rejects noncoincident pulses.

Solvent and sample component molecules in the sample matrix other than the analyte can interfere with the energy-transfer process. Some of the energy from the analyte may be dissipated when transferred to the solvent, and some may be transferred to sample components which are incapable of producing light. Interference from non-light producing processes or absorption of light within the solution is called quenching, and increases at higher concentrations.[28] Equation 1 describes the quenching process for the former type of quenching. The latter, results from absorption of some of the light by the sample, as it is propagated through itself toward the detector.

$$A^* + Q \rightleftharpoons (AQ)^* \rightleftharpoons A + Q + \text{heat} \qquad (1)$$

where: A = analyte in the ground state

A* = analyte in an excited state

Q = solvent molecule

The efficiency relates the number of disintegrations (events) which occur in a sample to the number which are detected. Efficiency is expressed as a percentage and is calculated using equation 2.[29]

$$E = \frac{cpm}{dpm} \times 100\% \qquad (2)$$

where: E = efficiency

cpm = counts per minute

dpm = disintegrations per minute detected

Even the analyte can quench itself. For example, uranium samples are often yellow and hence absorb some light. It is important to realize that all samples undergo some degree of quenching, necessitating steps to minimize its effect or correct for it.

Another interference which may occur when counting alpha, beta, or gamma particles is self-absorption.[30] If a flux of particles passes through matter, the number of particles emerging from the other side is diminished with increasing thickness of the absorber. The upper limit at which self-absorption occurs can be identified by successively increasing the concentration of carrier (i.e., nonradioactive isotopes of the analyte) in a series of samples having equal activity. Ideally, the concentration at which

the count rate diminishes within the desired precision decreases detectably should not be exceeded in an experiment; otherwise, a self-absorption correction curve is required.

Counting statistics

Another practical consideration essential to making an accurate measurement of activity, is an understanding of basic statistics involved in counting radioisotopes. Radioactive decay is a random process, so application of statistical rules is necessary to arrive at a mean counting rate; that is, the number of disintegrations which will probably occur in a given time.

In counting statistics, a Gaussian approximation (normal distribution) is used. The width of the distribution curve is the variance, and is equal to the mean count. The square root of the variance is the standard deviation, σ. There is a 68.3% chance that the measurement will differ from the mean, which is unknown, by less than σ.[31] This 68.3% confidence limit is called the random error percent, and its practical significance is that 10,000 total counts (irrespective of the time required to obtain these counts) must be obtained for each sample in order to maintain the random error at 1 %.[32] Additionally, the background counts must be significantly lower than the sample counts.

There is also an upper limit to the number of counts one should obtain in a certain time. If the counting rate (counts per second) is very high, one should be aware of the possibility of pulse pile-up. Pulse pile-up occurs as a result of limitations in the speed at which the detector may operate. If photons impinge upon the photocathode too rapidly, the pulse and accompanying electronics

will overlap due to electronic limitations. Also, there is dead time in the multichannel analyzer and other instrumentation. For these reasons, the activity should be considered when preparing samples, so that sufficient dilution may be achieved.

Atomic absorption and atomic emission

Atomic spectroscopy may be used for both qualitative and quantitative determination of about 70 elements, typically metal atoms.[33] Characteristic sensitivities lie in the parts per billion (ppb) range with limits of detection (LOD) at the nanogram level.[34]

A schematic illustrating the chemical processes involved in these measurements appears in Figure 1. A sample solution is aspirated into an air/acetylene or N_2O flame (1800-3200 K) which desolvates, vaporizes, and breaks the analyte down into clouds of neutral atoms. In the emission mode, the flame then provides thermal energy to excite the neutral atoms. The excited atoms return to the ground state, emitting light at wavelengths characteristic of the analyte, whose intensity is proportional to the concentration of the analyte in the flame. Photons generated in the decay of the excited analyte are measured in atomic emission. In atomic absorption, the energy source for excitation is a hollow cathode lamp (HCL). Light from the HCL passes through the neutral atom cloud, which may absorb some of the photons. The intensity of the light propagated through the sample is measured; therefore, the actual measurement is transmission. The transmission is related to absorbance by Beer's Law, given in equation 3.

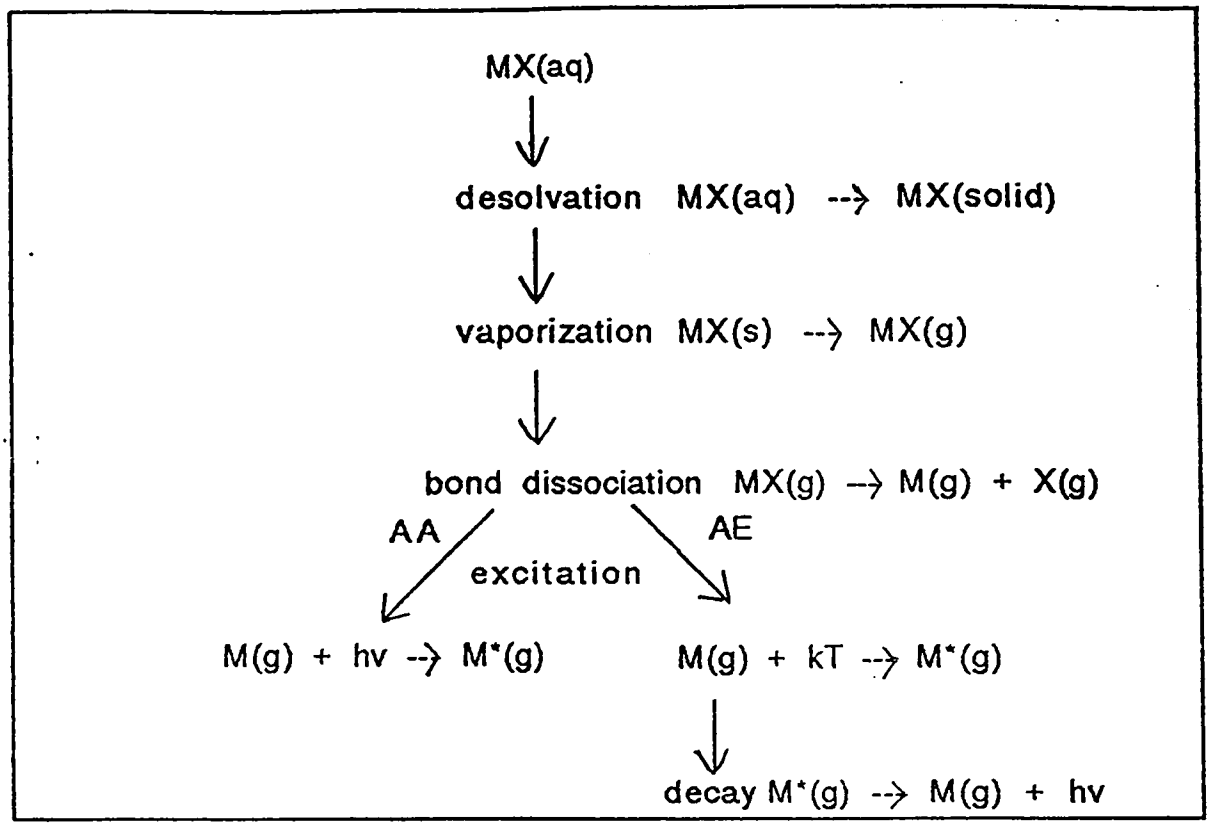


Figure 1. Schematic of the fate of the analyte in flame atomic absorption and atomic emission spectroscopy. M = the analyte atom, X = counter ion, hv = photon, kT = heat, AA = atomic absorption, AE = atomic emission.

$$A = \log \frac{P_O}{P} = Ebc \qquad (3)$$

where: A = absorbance

P_O = energy of the incident radiation (ergs) per second

P = energy of the radiation impinging upon the detector (erg/second)

E = molar absorbtivity ($L\ cm^{-1}\ mol^{-1}$)

b = length of the light path through the flame (cm)

c = analyte concentration (moles/L)

The amount of light absorbed by the analyte depends on the absorption coefficient (E), the length of the light path through the flame (b), and the analyte concentration (c). The relationship between absorbance and concentration, and these terms is illustrated in Beer's Law, equation 3. Actual quantitation is obtained using calibration standards.

OVERVIEW

Fundamental observations encountered during the development of SIR preparative techniques, and results from the application of selected extraction systems are presented in the chapters which follow. Experiments were performed by weighing beads into plastic scintillation vials, and contacting with dilute metal nitrate solutions for a pre-determined time interval. A fraction of the metal in the contact solution consisted of radioactive isotope. The solution was sampled after contact, and counted on a scintillation spectrometer. Data are presented as distribution coefficients, which are calculated using equation 4.

$$D = \frac{\dfrac{\dfrac{C_R}{t_R} - \dfrac{C_{BR}}{t_{BR}}}{w}}{\dfrac{\dfrac{C_A}{t_A} - \dfrac{C_{BA}}{t_{BA}}}{V_A}} \qquad (4)$$

where C_R = uncorrected counts in the resin phase

C_A = uncorrected counts in the aqueous phase

C_{BR} = background counts in the resin phase

C_{BA} = background counts in the aqueous phase

t_R = time resin phase was counted (seconds)

t_{BR} = time resin background was counted (seconds)

t_A = time aqueous phase was counted (seconds)

t_{BA} = time aqueous background was counted (seconds)

V_A = volume of aqueous phase counted (mL)

w = mass of dry resin (g)

All of the polymers used in this work were prepared from polystyrene 2.0 % divinylbenzene (DVB) crosslinked gel beads. Both polystyrene and functionalized polystyrene beads were used as supports for the SIRs, and one of the polymers in all the IPNs was also the polystyrene 2.0 % DVB crosslinked gel bead. Structures are shown in Figure 2.

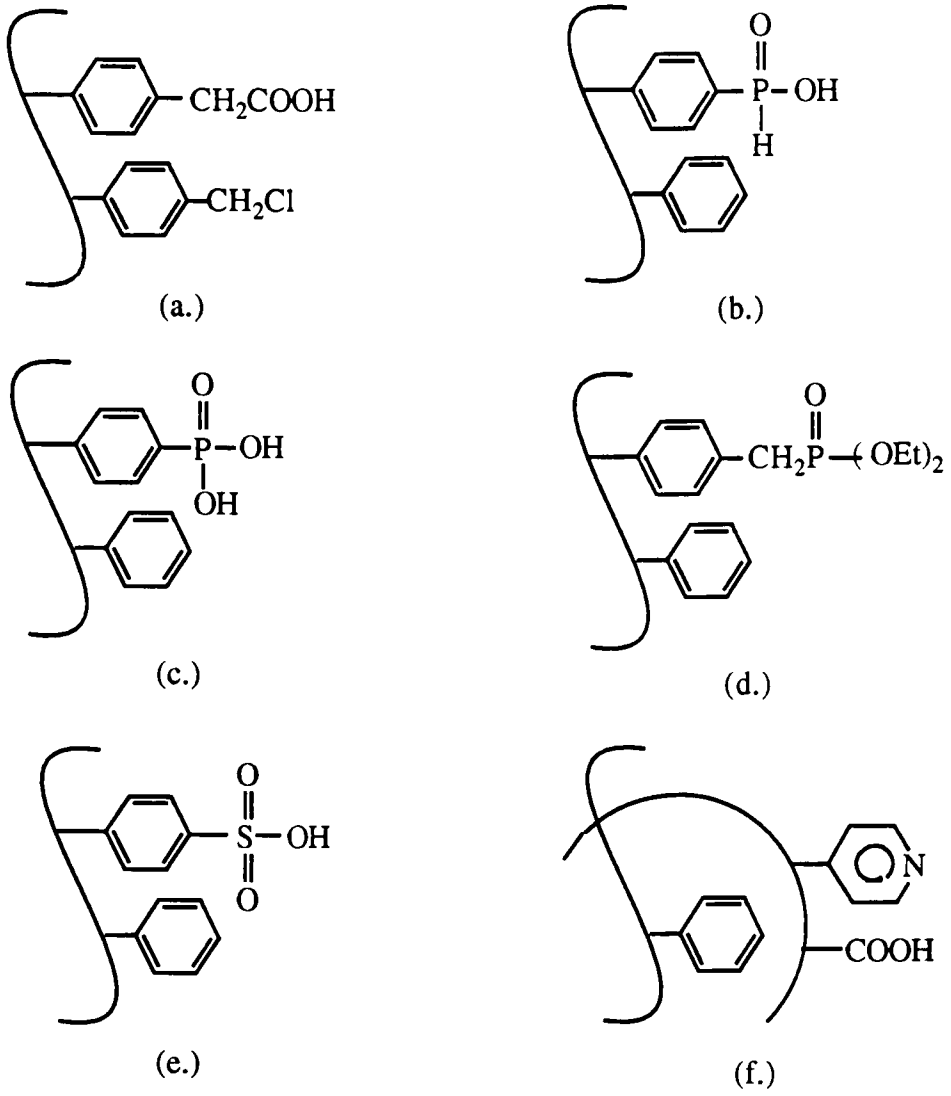


Figure 2. Structures of resin beads: (a.) partially functionalized carboxylic acid resin (COOH), (b.) partially functionalized phosphinic acid resin, (c.) partially functionalized phosphonic acid resin, (d.) partially functionalized diethylester resin (DE), (e.) sulfonic acid resin (SO_3H), (f.) vinylpyridine/acrylic acid interpenetrating polymer network (bif).

CHAPTER II

SOLVENT IMPREGNATED RESIN HANDLING: CHARACTERIZATION AND TECHNIQUE DEVELOPMENT

INTRODUCTION

Solvent impregnated resins (SIRs) were developed in response to a need for selective extracting reagents. They combine the desirable features of both solvent extraction and ion exchange. The polymer support offers high mobility and physical and chemical stability, so the unique selectivities afforded by many solvent extraction systems can be exploited without encountering difficulties of phase separation. Background information about these reagents is detailed in chapter one.

Several aspects of the extraction system must be considered when using SIRs: An appropriate impregnation method must be selected, rehydration kinetics and metal ion equilibration intervals must be determined and a proper mixing method must be chosen. Bead fragmentation, incomplete rehydration and insufficient mixing times produce scattered results in metal-ion studies.

Insoluble supports offer ease of separation of reactants from products, but the ligands which are incorporated into the beads must not partition significantly to the aqueous phase. It is, therefore, necessary when extracting the analyte from aqueous solution to select hydrophobic compounds as impregnates. Impregnation may be accomplished by a number of methods. The most common is the *dry impregnation method.*[35] This entails mixing dry resins in a

ligand-containing solution followed by evaporation of the solvent.[36] Another alternative is the *wet impregnation method.*[37] A solvent in which the polymer has good swelling properties is selected, a liquid extractant is added to the solvent, and enough resin to absorb all of the liquid is used. The *modifier addition method* involves introduction of a modifier which promotes water penetration into the resins, such as dibutyl-polypropylene glycol, followed by solvent evaporation.[38] SIRs used in this work were prepared by either wet or dry impregnation techniques.

EXPERIMENTAL

Bead impregnation

For the *dry method,* Buchner-dry resins were mixed four times, 15 minutes at a time, with methanol, and twice with acetone followed by 12-17 hours of drying in vacuo. A solvent is selected in which the beads have reasonable swelling properties, and a ligand is then dissolved in that solvent. Beads are mixed with an excess volume of the solution. In a parallel control test, an amount of swelling solution equal to the volume of solution equilibrated with the beads is emptied into a Buchner funnel and collected in a pre-weighed flask. The flask is placed on a rotary evaporator to remove the solvent, and the flask containing the residue is weighed to determine the weight of ligand in the initial solution. After equilibration, the beads are likewise emptied into a buchner funnel, and the excess swelling solution is collected in a pre-weighed Erlenmeyer flask. The solvent is removed from the flask using a rotary evaporator, and from the beads in vacuo. The flask is weighed again, and the amount of ligand sorbed by the beads is determined by difference.

The *wet method* is similar except more careful selection of the solvent and control of the volume used is required. An aliquot of swelling solution is added to the beads such that all of the solution is absorbed. The amount of ligand impregnated is known from the initial quantity of ligand used. Polystyrene resins which are used as experimental controls are swollen in the ligand-free solvent, then placed under vacuum so that treatment of the controls is identical to treatment of the SIRs.

A third method of impregnation uses Buchner-dry instead of vacuum dry resins and otherwise follows the dry method.

Batch reproducibility study

Realizing the differences in ligand loading in SIRs obtained using the different swelling techniques, it was of interest to determine whether or not two separate batches of SIRs prepared using the same impregnation method produce the same results. This was accomplished by performing a batch reproducibility study. The wet method was employed to prepare two batches of carboxylic acid beads impregnated with di-n-hexylsulfide (COOH/DHS) SIRs. A partially functionalized COOH resin (75.4 % solids and acid capacity = 1.49 mequiv OH/g dry beads) was rinsed four times with methanol for 15 minutes and twice with acetone. The beads were placed under vacuum for 16 hours. Two fractions of vacuum dry beads (1.96 g and 1.17 g) were weighed into graduated test tubes with 0.06 g DHS and 0.06 g DHS respectively, in 4.5 mL p-dioxane (99.9 %, E M Science, Gibbstown, N.J.). The vessels were sealed with teflon-lined screw-on caps and slowly rotated (26 rpm) on a disk at an angle of 45° for six hours, when all of the liquid appeared to have been absorbed.

Resins were then placed under vacuum for 17 hours. Vacuum dry resins were then weighed into vials and mixed with nanopure water for 144 hours. A matrix solution was prepared by adding boric acid (analytical grade, Mallinckrodt) to give a concentration of 0.10 N in the final volume, $NaNO_3$ (analytical grade, Mallinckrodt) to give 0.2 N in the final volume, and the pH was adjusted to 10.0 using 50 % NaOH (analytical grade, J. T. Baker, Inc.). Resins were agitated with the matrix solution three times for 15 minutes, removing the solution with a pasteur pipette each time and replacing with fresh solution. A fourth aliquot was mixed with the beads for one hour, after which 2.0 mL of a metal-containing solution was added. The metal-containing solution was prepared identically to the matrix, except enough $Hg(NO_3)_2$ (99.0 %, MCB Manufacturing Chemists, Inc., Cincinnati, OH) to produce a concentration of 1.0×10^{-4} N in the final volume, with a small volume of Hg-203 (New England Nuclear) was added to this solution. Samples were equilibrated for 66 hours at ambient temperature (23 ± 2 °C) after which the aqueous phase was assayed by gamma spectrometry.

Solvent dependence study

To examine the ligand loading dependence upon the swelling solvent selection, two kinds of SIRs were prepared using two different solvents. A 0.70-M solution of TBP (tributyl phosphate, analytical grade, BDH Chemicals, Ltd.) in toluene (high purity, Baxter Healthcare Corporation, Muskegon, MI) and a 0.70-M solution of TBP in ethanol (absolute, AAPER Alcohol and Chemical Co., Shelbyville, KY) were prepared. Aliquots of 5.0 - 10.0 mL were measured into equilibration vessels with a known weight of vacuum-dry synthetic polystyrene 2.0 % divinylbenzene (DVB)-crosslinked beads or partially

functionalized (25%) phosphinic acid beads. Beads and swelling solution were mixed, and an initial volume of beads was measured using a graduated test tube. Resins were equilibrated with the solutions for 24 hours after which a final volume reading was measured. The swelling ratio (SR) was obtained by dividing the final volume occupied by the beads, by the initial bead volume. The remaining liquid was collected in a pre-weighed Erlenmeyer flask. Quantitation of sorbed ligand was obtained gravimetrically as in the batch reproducibility experiment detailed above.

Bead fragmentation study

An investigation of sources of irreproducible results showed that in some cases, fragmentation of the beads occurs. This was illustrated using phosphinic acid resins which were equilibrated 17 hours on an Eberbach shaker (Ann Arbor, Michigan) with 1.0×10^{-4}-N $Eu(NO_3)_3$ (analytical grade, Aldrich) in 1.0-N HNO_3, 0.10-N HNO_3, and 0.010-N HNO_3 (analytical grade, J. T. Baker Inc.). The solution also contained a spike of Eu-152/154 radiotracer (Oak Ridge National Laboratory, Oak Ridge, TN). After equilibration, the aqueous phases were transferred to clean scintillation vials, and some of the vials were centrifuged for 15 minutes at about 10 G. An aliquot of the aqueous phase was transferred to another scintillation vial and assayed by gamma spectrometry.

Complexation kinetics study

Resins stored in water were Buchner dried for 5 minutes at 10 mm Hg. Enough resin to produce 1 mequiv of ligand sites was weighed into vials. A metal ion solution was prepared by combining $Zn(NO_3)_2$ (analytical grade, J. T. Baker, Inc.) to yield a final concentration of 1.0×10^{-4} N, enough acetic acid (glacial,

analytical grade, Mallinckrodt) to produce a concentration of 0.60 N in the final volume, and Zn-65 radiotracer (New England Nuclear, Billerica, MA). Three milliliter aliquots of the metal ion solution were mixed with the beads for different lengths of time. A subsample of the aqueous phase was counted on a gamma spectrometer equipped with a NaI well-type detector.

Rehydration

Another factor which influences experimental precision is rehydration. This conclusion arose from experimentation with vacuum dry, partially functionalized carboxylic acid resins, which were placed in water for varying lengths of time. The water was removed with a Pasteur pipette, and a Hg-203 (New England Nuclear) tracer-containing solution of 1.0×10^{-4} N $Hg(NO_3)_2$ (99.0 %, MCB Manufacturing Chemists, Inc., Cincinnati, OH) was introduced. All of the samples were equilibrated at ambient temperature with the metal-ion solution for 70 hours on a rotating disk at 26 rpm.

In the same manner as the unimpregnated resins, the SIRs must undergo the rehydration process prior to metal-ion extraction experimentation. Because the COOH resin behavior a showed strong dependence upon degree of rehydration, it was necessary to evaluate the resins before and after rehydration and to determine the fate of the sorbed ligand.

Dry impregnation was employed to sorb tetrathia-14-crown-4 (TT14C4) (analytical grade, Aldrich) to polystyrene and sulfonic acid beads. Buchner dry beads were mixed four times for 15 minutes with methanol and twice with acetone. The beads were vacuum dried for 12 hours at 25 ^{o}C.

Dry polystyrene 2.0 % DVB crosslinked beads (7.61 g) were washed with p-dioxane (reagent grade, E. M. Science) four times for 15 minutes, removing the solvent after each equilibration cycle and replacing with fresh dioxane. A 0.16-M solution of TT14C4 in dioxane was then prepared, and 15 mL of this solution was mixed with the PS beads on the Eberbach shaker. The beads were allowed to equilibrate with the solution for 18.5 hours after which resins were emptied into a Buchner funnel mounted atop a bell jar connected to vacuum. The remaining solution was collected quantitatively in a pre-weighed flask inside the bell jar. The dioxane was removed from the flask using a rotary evaporator, and the flask containing the residue was weighed. Using the difference in these two weights, the amount of ligand incorporated into the polymer was calculated. The resins were transferred to three clean glass scintillation vials and placed in a vacuum oven at 25 ^{o}C for 12 hours. A small portion of polystyrene was washed with dioxane and was not contacted with the thia-ligand but was otherwise treated identically to the SIR beads to serve as a control for the experiment.

Vacuum dry SIRs were contacted four times for one hour with nanopure water. The mixing was done on the Eberbach shaker. Following each cycle of the rehydration, the rinse water from all three vials was emptied through a single millipore filter (6 μm) and the filtrate was collected in a clean flask. The water appeared cloudy on rinses 1-3, and the fourth rinse was clear. The water was allowed to evaporate in the hood. The walls of the flask were coated with a white film, but nothing was observed on the millipore filter. There was also no change in the mass of the filter after filtration. When the water had evaporated from the flask, the walls were rinsed with methanol and acetone to

ensure removal of the water and to concentrate the film on the base of the flask. A very small quantity was scraped from the flask with a clean spatula and was ground in a mortar with dry KBr. A pellet was then pressed and the residue analyzed by FTIR (Bio-Rad FTS-60, Bio-Rad, Cambridge, MA). For comparative purposes, spectra of polystyrene and TT14C4 were also obtained.

The rehydrated beads were filtered in a Buchner funnel for 10 minutes at 10mm Hg, with air passing through the funnel. The resins were stirred with a spatula to ensure homogeneity of the sub-sample, and a portion was removed and added to a pre-baked, pre-weighed glass vial which had been cooled in a desiccator. The weight of the vial and wet beads was measured, and the sample was oven-dried for 17 hours at 110.0 °C. A final weight was taken, and the percent solids was calculated using equation 5.

$$\% \text{ solids} = \frac{\text{oven dry weight of beads (g)}}{\text{Buchner dry weight of beads (g)}} \times 100 \qquad (5)$$

Samples of PS (solvent washed), PS/TT14C4 before and after rehydration, solvent washed SO_3H, and SO_3H/TT14C4 before and after rehydration were sent to Galbraith Laboratories (Oak Ridge, TN) for carbon and sulfur elemental analyses. Analysis of each type of SIR was requested in duplicate.

Acid capacity

The procedure for determining the acid capacity of resin beads involves weighing 1.0 g - 1.5 g of Buchner-dry resins into a ground glass Erlenmeyer

flask. Standardized 0.10-N NaOH solution (200.0 mL) which is also 5.0 weight percent NaCl, is mixed with the beads for 12 hours on a stir plate. A 50.0 mL aliquot of the NaOH solution is then titrated with 0.10 N - 0.15-N H_2SO_4 to a phenolphthalein endpoint. The total acid capacity is calculated as in equation 6.

$$\text{total (OH)} = \frac{(\text{total mL NaOH})(\text{N NaOH}) - 4(\text{N } H_2SO_4)(\text{mL } H_2SO_4)}{\text{weight vacuum dry resin (g)}} \qquad (6)$$

The coefficient , 4 , accounts for the reduced volume of the titrated sample (50.0 mL of the 200.0 mL is titrated).

Resin-phase counting procedure

For experiments using a gamma-emitting metal isotope, the counting procedure depends upon the nature of the beads. Due to the viscous nature of some liquid extractants, SIRs prepared using these are often sticky. For very sticky SIRs, the aqueous phase was sampled, and a glass wool plug was inserted in the vial. The suction device illustrated in Figure 3 was used to remove the remaining liquid. The beads were rinsed three times with an appropriate matrix, for example, when operating at pH 5.0, water was used. Each time, the liquid was rapidly removed to prevent stripping of the metal. A clean cap was inserted in the vial, and resins were then counted on a NaI gamma spectrometer. If the beads were not too sticky to prevent a quantitative transfer, the resins and aqueous phase were emptied into a clean vial and rinsed three times as were the sticky beads. In all cases, the contact solution was equilibrated in a parallel fashion, sampled, and counted to provide an

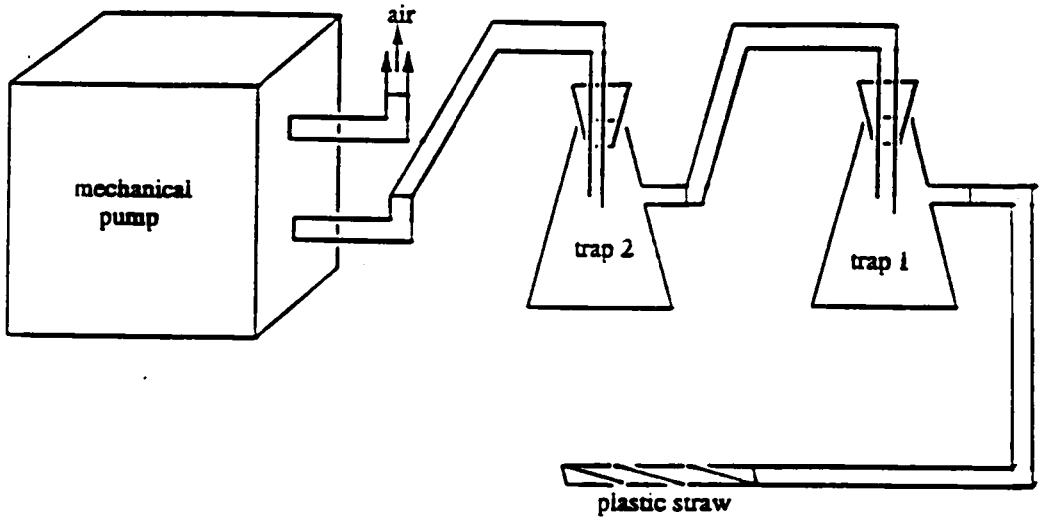


Figure 3. Suction apparatus for removal of aqueous phase from resins

initial activity for mass balance determination. The mass-balance (MB) is expressed as a percentage and is calculated as in equation 7.

$$\% \text{ mass balance} = \frac{C_r + C_a}{\text{i. a.}} \qquad (7)$$

where C_r = number of counts per minute in the resin phase

C_a = number of counts per minute in the aqueous phase

i. a. = number of counts per minute in the contact solution

RESULTS AND DISCUSSION

An advantage of the *wet impregnation* method is that close control of ligand loading is possible. Simply varying the ligand concentration in the swelling solution ensures a corresponding change in ligand loading of the beads. Additionally, because less reagent is necessary for this impregnation method, valuable ligands are conserved and a limited volume of hazardous waste is generated. A disadvantage of employing this method is the necessity of assuming that all of the ligand in the swelling solution is incorporated by the beads when determining ligand loading. This is probably a reasonable assumption, however, more ligand may be associated with the outside of the beads using this technique rather than the dry method. Swelling occurs very rapidly (usually within minutes if a proper solvent is selected) when limited solvent is available, so there is little time for partitioning of the ligand. Instead, the beads clump together in the equilibration vessel, and thus the ligand is probably less accessible to beads on the outer surface of the clump

while more centrally located beads can continue to swell and absorb ligand from the solution trapped in the interstitial spaces. This may lead to inhomogeneous absorption. Batch-to-batch precision has, nevertheless, been established using large sample sizes (0.20 g - 0.25 g, vacuum dry weight) with careful mixing prior to sampling the beads.

Table 1 presents metal $Hg(OH)_2$ distribution data obtained using two separately prepared batches of SIRs. The contact solution was 1.0×10^{-4} N $Hg(NO_3)_2$ initially at pH 10.0 in 0.10-N boric acid. The very good agreement between log D values illustrates that possible inhomogeniety produces no detectable irreproducibility under the equilibration and sampling procedures employed.

TABLE 1

COOH/DHS SIR PERFORMANCE AMONG DIFFERENT BATCHES

resin sample	log D
batch 1	2.52
batch 1	2.56
batch 2	2.54
batch 2	2.59

The *dry impregnation* method is the most commonly used technique for sorbing a ligand into a polymer support. Mixing the dry resins with an excess volume of solvent provides this method with several advantages over other techniques. The excess solvent keeps the beads suspended during

equilibration, so uniform partitioning of the ligand can occur. A gravimetric analysis is possible with this method, so very accurate sorption data are available. Less control, however, over the ligand loading is possible because this parameter is highly dependent upon the choice of solvent and certain conditions (concentration of water), and also because one does not know in advance how well the ligand will partition into the resin.

TABLE 2

LIGAND LOADING DEPENDENCE ON SOLVENT

SIR	solvent	swelling ratio	gravimetry
PS/TBP	ethanol	1.0	not analyzed
PS/TBP	toluene	1.7	0.47 g TBP per g SIR
phos/TBP	ethanol	1.32	0.10 g TBP per g SIR
phos/TBP	toluene	1.34	0.03 g TBP per g SIR

The swelling ratio (SR) is defined as the ratio of the final volume of the beads after swelling to the initial volume of the beads. As given in Table 2, the phosphinic acid/TBP (phos/TBP) SIRs have similar swelling ratios in toluene and ethanol but gravimetry indicates the amount of ligand sorbed by the beads differs considerably. Polystyrene readily swells in toluene, but not at all in ethanol. This illustrates the variability of ligand loading encountered using the dry impregnation method. If time for solvent experimentation is

abundant, however, this feature can be exploited to obtain very high or very low loadings.

Another impregnation method, which is very similar to the dry method, uses Buchner-dry beads rather than vacuum dry-beads. In this alternative method, the Buchner-dry beads are contacted with the solvent for a short time prior to mixing with the ligand-containing solution. Filtration and evaporation follow, as with the dry method. Lower ligand loading has been reported using this technique than was obtained in the same SIR system under similar conditions employing the dry impregnation method.[39] This is a reasonable result considering the more hydrophilic regions of the polymer still contain water upon ligand contact. In these regions of the polymer, the hydrophobic ligand is repelled and the overall sorption is less. This same reason contributes to inhomogeneity, however, this method does not require drying of the beads under vacuum and thus reduces experimental time by at least 24 hours.

Figure 4 summarizes the procedures for resin handling from synthesis to experimental application of the SIR. After SIR preparation is completed, several experiments are necessary to ensure good results are obtained in a metal ion extraction study. An important aspect to demonstrate is that fragmentation of the beads does not occur over the course of an experiment. This can be tested using centrifugation. Figure 5 shows very good agreement among centrifuged samples while values of log D for uncentrifuged samples are erratic.

If bead fragmentation occurs, fragments may be removed with the aqueous

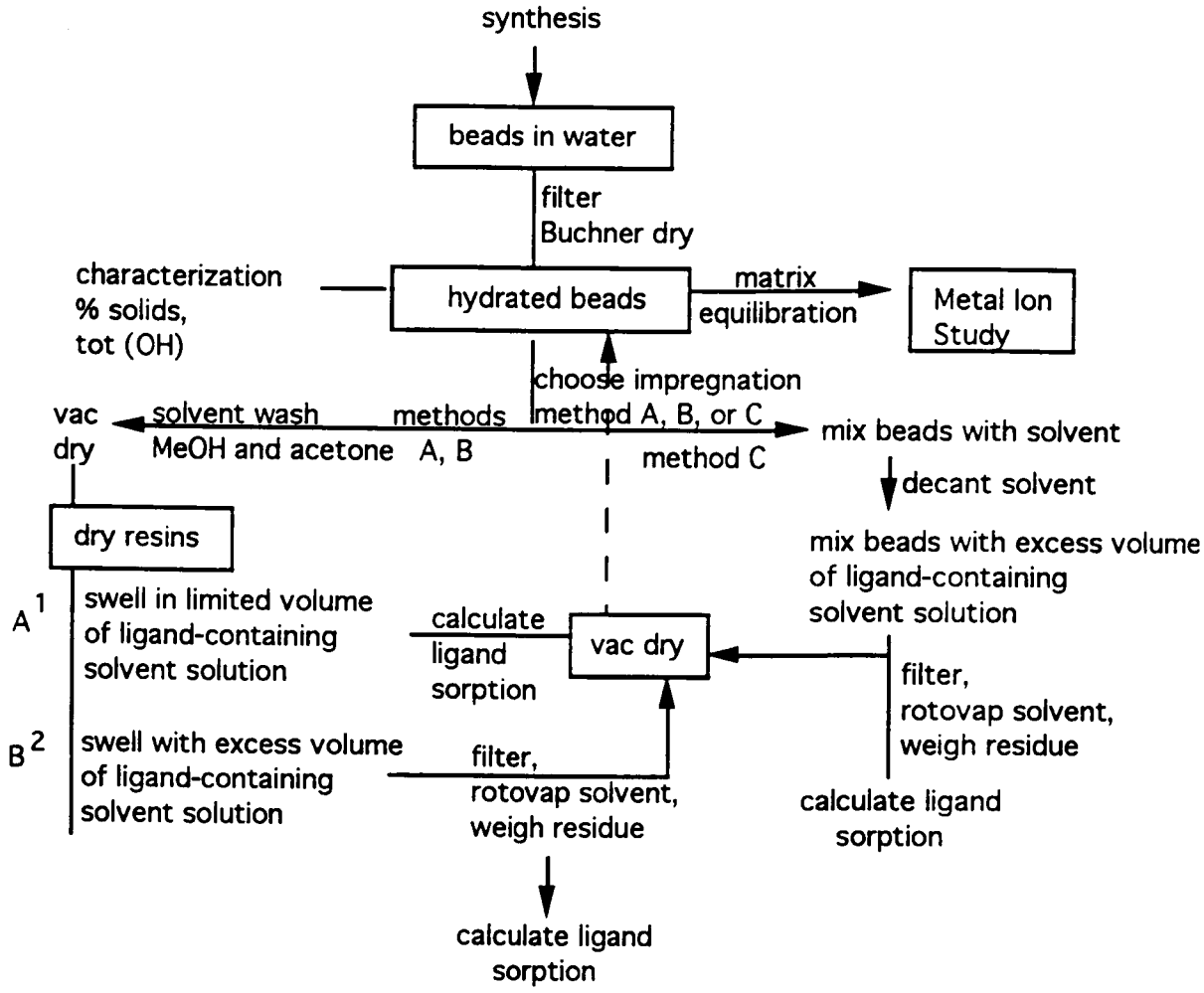


Figure 4. Schematic for the preparation and handling of solvent impregnated resins. [1]wet impregnation method; [2]dry impregnation method

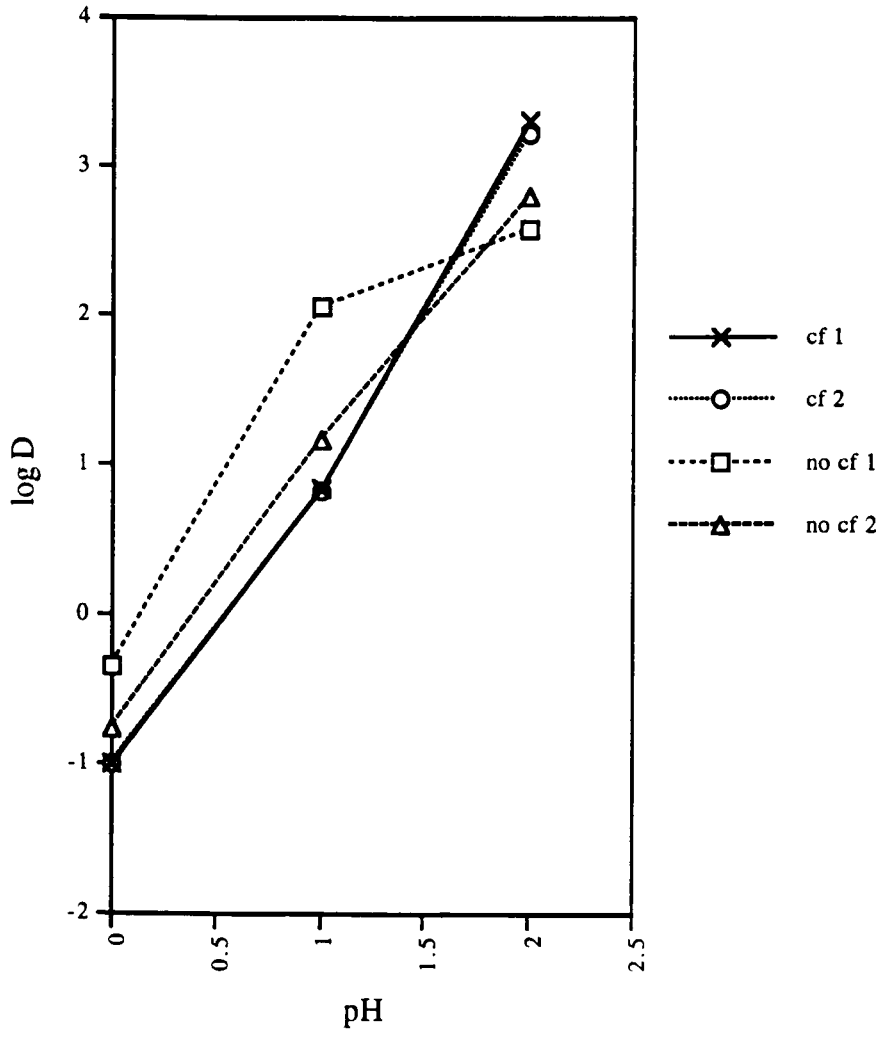


Figure 5. The effect of centrifugation of phosphinic acid resins after metal ion equilibration. Samples contained about 0.20 g of phosphinic acid resins, and were equilibrated for 17 hours with a 1.0×10^{-4} N solution of $Eu(NO_3)_3$ adjusted to pH 0.0, 1.0, and 2.0 with 2.0 N HNO_3.

aliquot if samples are not centrifuged. Additionally, activity which may be associated with fragments may remain in the organic phase introducing an inherent error in the resin measurement. All the metal counted in the resin phase, would then, not be bound by the polymer functionality.

The Eberbach shaker action is a quite vigorous motion on a horizontal plane. A gentler means of mixing may eliminate fragmentation in some cases, however, some beads are more suseptible to fragmentation than others. Crosslinking, for example, increases the mechanical strength of polymers, thus reducing the probability that fragmentation will occur. Slight fragmentation has been observed during the rehydration cycle, so it is also important to rehydrate the beads prior to metal ion equilibration.

A property of the extraction system which must be considered is kinetics. Reaction kinetics are very much a function of the resin used; however, pre-equilibration with the matrix solution slightly accelerates the process. Figure 6 illustrates that equilibrium between a bifunctional vinylpyridine/acrylic acid polymer and a zinc-containing aqueous solution occurs after about 24 hours. This is indicated by a leveling off of the distribution coefficient. The curve in the figure has been smoothed, using the dotted line, because kinetic plots are generally $1 - e^{-x}$ functions. If nothing is known about the polymer, it is necessary to equilibrate for a much longer time, perhaps more than a week, to determine when the system reaches equilibrium and that no secondary reactions strip metal from the polymer. A kinetic study must be done for each system under investigation.

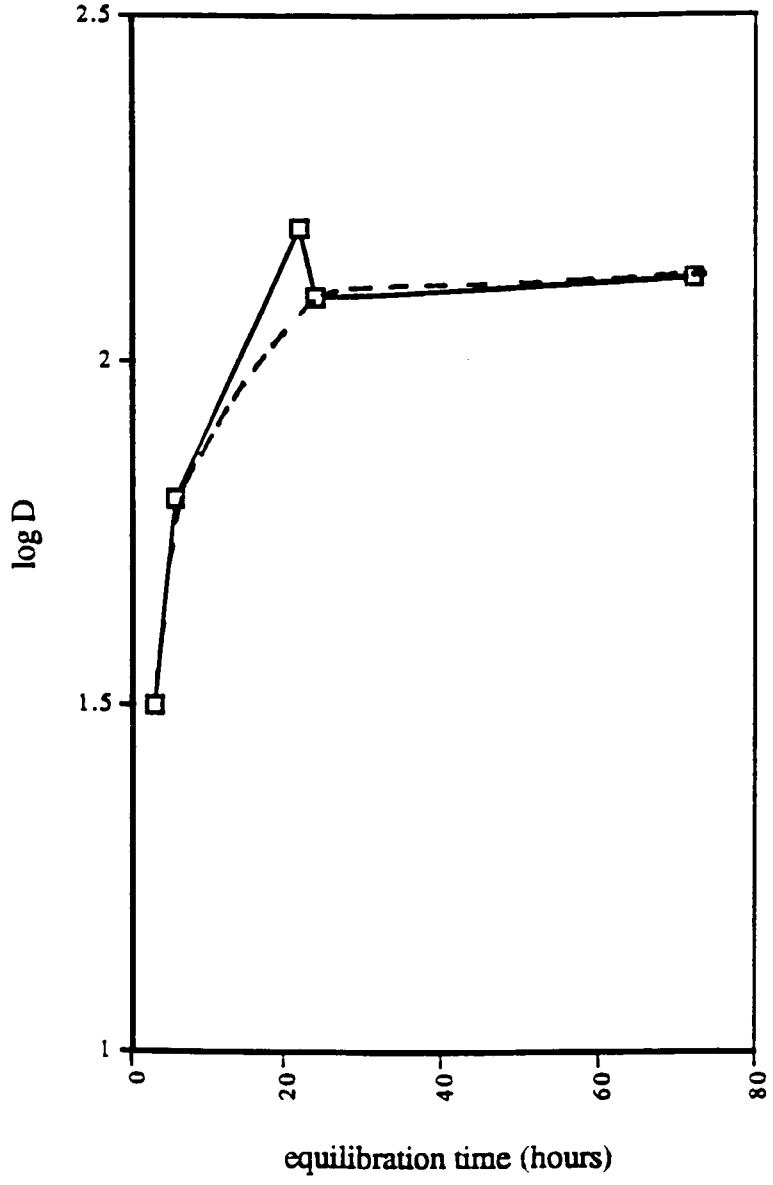


Figure 6. Kinetic study of a bifunctional vinylpyridine/acrylic acid polymer with a dilute zinc nitrate solution at pH 6.0.

It was found that prior to metal ion experimentation, complete rehydration of the SIRs is an important process. Although the samples were not pre-equilibrated with the matrix, Table 3 clearly shows extraction increases as the length of the rehydration interval increases. When vacuum dry, the beads collapse, and must be allowed sufficient time to re-swell for optimum reactivity. The time required to fully rehydrate resins depends on the hydrophilicity of the ligands and on the degree of functionalization of the polymer.

TABLE 3

THE EFFECT OF INCOMPLETE REHYDRATION OF POLYMER BEADS

ON METAL ION EXTRACTION

Rehydration Interval (hours)	log D
6	0.91
6	1.01
17.75	1.18
17.75	1.09
23	1.13
23	1.09
48	1.28
48	1.30

Since the transition from dry, collapsed beads to fully rehydrated beads entails physical change in the bead, the fate of the ligand within the polymer was questioned. Further questions arose when during an experiment using sulfonic acid and PS resin beads impregnated with TT14C4 (dry impregnation method), precipitate was observed in the rehydration vessels. FTIR spectra of

the precipitate showed that a very small amount of material that apparently evacuates the beads during rehydration consists at least partly of TT14C4, so SIR samples before and after rehydration were analyzed by Galbraith Laboratories (Knoxville, TN), and the results were compared with gravimetric data. Gravimetric analysis showed the macrocycle loaded on the PS was 0.04 g TT14C4/g SIR. The elemental analysis (before rehydration) reports the loading to be 0.02 g TT14C4/g SIR. For the sulfonic acid-thia-crown beads, gravimetry gave 0.14 g TT14C4/g SIR and elemental results show 0.12 g TT14C4/g SIR. The results are consistent. There is also fairly good agreement between the sulfur content in the SO_3H control, assumed to be equivalent to the acid capacity of the SO_3H beads (1.57 mmol/g), and the elemental analysis reports 1.21 mmol S/g beads. Results appearing in Table 4, show that more macrocycle is present in the SO_3H/TT14C4 beads after rehydration than is present before water contact. Given the experimental error suggested by the poor agreement between duplicates, and the probable inhomogeneity of the sorbed ligand within the polymer matrix, the difference in these numbers is not surprising. Considering bead size variation and impregnation method, it is likely the thia-macrocycle aggregates in the hydrophobic regions of the polymer and certainly some is associated with the outside of the beads. Using the dry-impregnation method, this inhomogeneity is probably even more pronounced because without excess solvent to keep all the beads suspended during mixing, the partitioning of the ligand cannot be uniform. The poor agreement between duplicate samples is especially noticeable in the sulfonic acid samples. Disagreement between the gravimetric and elemental analysis data is due to the small sample size used for combustion analysis. Less than 5.0 mg was

TABLE 4

ELEMENTAL ANALYSIS DATA OBTAINED FROM GALBRAITH LABORATORIES

sample	element	% element	duplicate
SO_3H-crown before rehyd.	C	75.70	74.40
	S	6.70	6.98
SO_3H-crown after rehyd.	C	72.93	73.24
	S	7.03	7.57
SO_3H	C	73.10	73.34
	S	4.21	4.76
PS	C	91.64	91.19
	S	<0.02	
PS-crown before rehyd.	C	86.39	86.13
	S	1.40	1.39
PS-crown after rehyd.	C	87.05	87.02
	S	1.41	1.37

used for the analysis. This corresponds to a very small number of beads and given the inhomogeneity of SIRs, the sample is not necessarily representative of the bulk. In summary, the gravimetric results are more reliable than the elemental analysis results, however, there was general agreement between the two methods. Of primary importance is that the data indicate that most (85 %) of the macrocycle in the resin beads survives rehydration.

In any separation, it is important to account for all of the analyte to unequivocally show no physical or chemical losses have occured. If the experiment employs a radiotracer, counting of both phases is required to show a mass balance. If the radiotracer emits beta particles, the resins must be stripped of metal using acid or base to adjust the pH to one at which the ligands no longer bind the metal. Stripping is necessary because some beta radiation cannot penetrate the polymer matrix. A scintillation cocktail must then be added to the stripped metal, to provide a fluorophor. Attempts to count beads stripped of metal using acid or base to adjust the pH to one at which the ligands no longer bind the metal. Gamma radiation is much more penetrating than beta particles, so in gamma tracer experiments, counting of the resin phase is possible without stripping the metal from the beads with acid or base. Elimination of this stripping step is desirable since losses can occur during this process. Other techniques to prepare beads for counting exist, such as ashing the beads in a muffle furnace followed by addition of the scintillation cocktail, or digesting the beads in concentrated nitric and perchloric acids, however, these were not practical in the laboratory which was used for the work in this thesis. Under most favorable conditions for transfer, the beads are not sticky and can, therefore, be quantitatively transferred to clean vials

where rinsing and counting occurs. The advantage of transferal of the sample to a clean vial for analysis is that a small amount of activity which sticks to the walls of the equilibration vessel is not incorrectly counted as part of the resin phase. Table 5 illustrates the mass balance obtained using the two methods for resin counting. Beads which are not sticky can be counted quite accurately as indicated by % mass balance values very close to unity. Resins used in this experiment were bifunctional interpenetrating polymer networks rather than solvent impregnates so are not even slightly sticky. Results from experiments using sticky beads are not quite as good, especially with the diethylester resin impregnated with Cyanex 272. Of all the SIRs presented in this thesis, however, the DE/Cyanex is by far the stickiest so this percent mass balance value represents a worst case scenario. Using non-sticky beads and a gamma emitting isotope are the simplest of conditions to work with, but either counting technique may be applied with reasonable confidence provided an initial activity measurement is made.

TABLE 5

ACCURACY OF ACTIVITY DETERMINATION OF ORGANIC AND AQUEOUS PHASES

NON-STICKY BEADS		STICKY BEADS	
sample	% mass balance	sample	% mass balance
VP/AA[1]	99	DE/Cyanex[2]	108
VP/AA	97	DE/Cyanex	89
VP/AA	100	phos/TBP[3]	101
VP/AA	100	PS/Cyanex[4]	102

[1]Bifunctional vinylpyridine/acrylic acid interpenetrating polymer network.

[2]Diethyl ester resin impregnated with Cyanex 272® (Cyanamid, Niagra Falls, Ontario)

[3]partially functionalized phosphinic acid resin impregnated with tributyl phosphate (BDH Chemicals, Ltd.)

[4]polystyrene 2.0 % DVB crosslinked resin impregnated with Cyanex 272®

CHAPTER III

APPLICATION AND EVALUATION OF SELECTED SIR SYSTEMS

INTRODUCTION

Europium(III) and uranium(VI) were the target ions for extraction studies reported in this chapter. Europium has several important industrial applications, such as phosphors, optical amplifiers, commercial dyes, and superconductors.[40-42] Because of its commercial value and relatively low natural abundance, isolation of europium is of interest.[43] Additionally, europium is useful as a substitute for trivalent actinides. Recovery of uranium is also important, because of its application as a nuclear fuel, and its great abundance in nuclear waste.[44]

Examples of solvent extraction of europium and uranium using numerous combinations of organophosphorus esters with liquid extractants such as Cyanex®, TTA, TBP and TOPO, are abundant in the literature.[45,46,47] These liquid extractants were, therefore, selected for sorption into diethylester resin beads.

EXPERIMENTAL

All stock metal-ion solutions were prepared at a low pH (1.0 or 2.0) to suppress hydrolysis. A stock solution of 1.0×10^{-3}-N $Eu(NO_3)_3$ was prepared by weighing europium(III) nitrate hexahydrate (99.99%, Aldrich) into a volumetric flask with sufficient 0.10-N nitric acid (analytical grade, J. T. Baker Inc.) to produce a concentration of 0.01 N in the final volume. Solutions to be

used for contact with resins were made by sampling the stock and diluting with enough nitric acid to produce the desired hydrogen ion concentrations. A spike of Eu-152/154, also in the nitrate form (Oak Ridge National Laboratory), was added for tracing the metal-ion partitioning.

A 0.07-M $UO_2(NO_3)_2$ stock solution of uranium-234/238 was prepared by slowly heating 1.01 g U_3O_8 (Amersham) in a crucible with 5.0 mL of concentrated nitric acid (analytical grade, Baker Chemicals). The liquid was heated to dryness, and 5.0 mL of nanopure water was added. Again, the liquid was heated to dryness, and the remaining solid was diluted to 50.0 mL with 0.01-N HNO_3. Additional solutions were prepared by diluting aliquots of the stock solution with nitric acid.

An extractive scintillation solution was prepared following the procedure developed by W. J. McDowell and co-workers.[48] To a 50-mL volumetric flask, 1.61 g di-2-ethylhexylphosphoric acid (Mobil), 10.0 g naphthalene (analytical grade, Fisher Scietific), and 0.20 g 2-4'-biphenylyl-6-phenylbenzoxazole (PBBO, Eastman Kodak Co.) were added. The mixture was diluted with toluene (high purity, Baxter Healthcare Corp., Muskegon, MI).

For analysis in experiments using uranium, 1.0 mL aliquots of aqueous uranium samples were shaken for 15 minutes with 1.5 mL of the extractive scintillator described above. When the phases had completely separated, exactly 1.0 mL of the equilibrated extractive scintillator containing U(VI) was removed and placed in a glass culture tube. The tube was sparged with

toluene-saturated argon gas for 2.0 minutes and was quickly corked. The vials were then assayed using a PERALS instrument.

Diethylester (diester) resins were impregnated with Cyanex 272® (Cyanamid Canada Inc., Niagara Falls, Ontario) by contacting dry resins with a 0.60 M Cyanex® solution in toluene on a rotating disk (12 rpm) for 27 hours. After the first six hours, a boundary, distinguishable by color, was observed. The two layers were sub-sampled and analysed for elemental phosphorus. Twenty one hours later, all beads were a uniform burnt orange color. Another SIR was prepared using the diester with 2-thenoyltrifluoroacetone (Columbia Organic Chemical Co., Columbia, S. C.) in toluene (high purity solvent, Baxter Healthcare Corporation, Muskegon, MI). The 2-thenoyltrifluoroacetone (TTA) was recrystallized by dissolving some of the compound in ethanol while gently heating with a hot plate, followed by dropwise addition of nanopure water until a few crystals formed. The flask was removed from the heat, and allowed to stand in the hood for almost one week. Crystals were vacuum filtered followed by drying in vacuo.

Prior to performing any studies with resins, several experiments were done to establish counting parameters and limitations within which the experimental conditions must conform when using europium. First, a test for self-absorption was done by counting a series of solutions containing Eu^{3+} concentrations ranging from 1.0 M to 5.0×10^{-5} M $Eu(NO_3)_3$, all in a constant volume of 1.0 mL. Three different peaks in the energy spectrum were monitored and allowed to reach 10,000 counts. The peaks were then examined

for an energy shift. The peaks no longer shifted at 5.0×10^{-4} M $Eu(NO_3)_3$ but were apparent at 1.0×10^{-3} M $Eu(NO_3)_3$.

If a sample is very large relative to the scintillator crystal, or sample placement is less than ideal, the proportion of gamma rays detected decreases. To test the effect of sample depth on counts, samples were prepared with constant activity, constant $Eu(NO_3)_3$ concentration, and varying volume. The results appear in Figure 7. Clearly, within the volume range tested, the effect is only weakly varying.

RESULTS AND DISCUSSION

Analysis of the two differently colored layers of diesters impregnated with Cyanex® showed that sorption of the Cyanex® was not uniform. The top layer had a phosphorus capacity of 5.50 meq P/g resin, while the lower burnt orange-colored layer had lower P content, 3.69 meq P/g resin and 3.87 meq P/g resin. With longer contact times and mechanical mixing, a single color was obtained, suggesting uniform absorption of the ligand. The uneven distribution initially present during the swelling cycle was likely caused by size differences among resins. Without mechanical mixing, density of the smaller beads approaches that of the swelling solution and the resins float, achieving maximum exposure to the ligand while larger beads in the base of the vessel had limited access to the solution. The diester/Cyanex SIR was evaluated for europium extraction at pH 1.0 and pH 2.0.

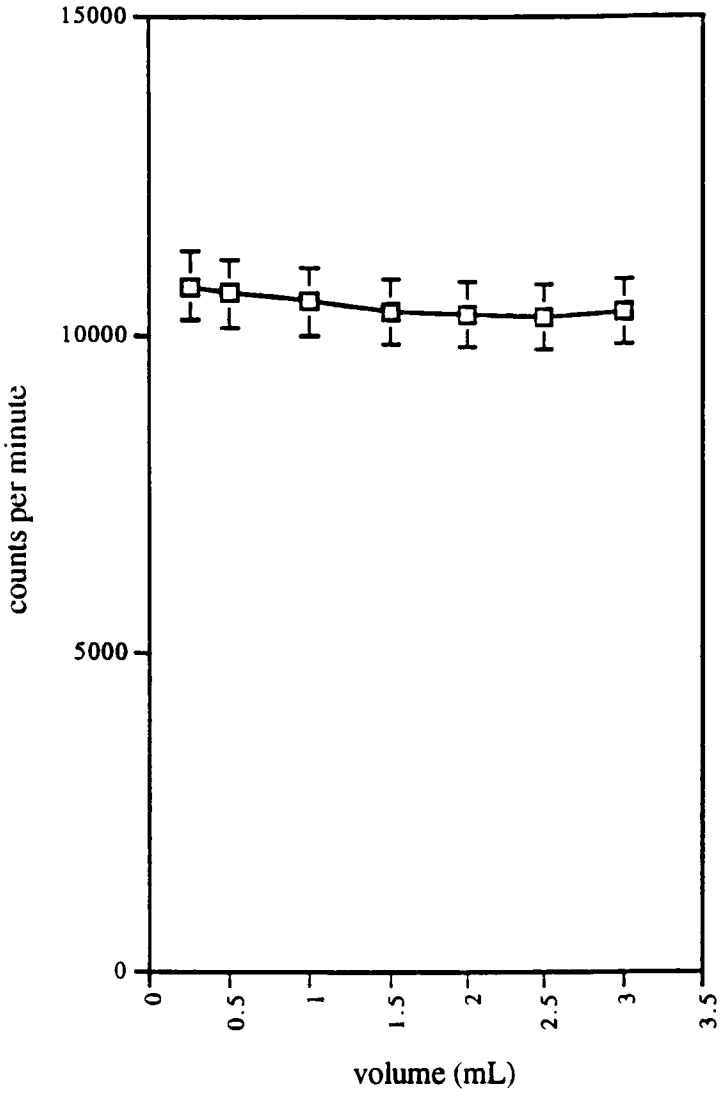
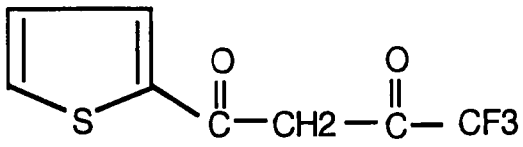


Figure 7. Depth calibration curve. This plot illustrates the effect of sample depth on detector response.

Table 6 suggests a slight synergistic effect operating at pH 2.0 with the DE/Cyanex. A much greater degree of synergism was desired, so this system was not explored further. Instead, the diester and polystyrene were impregnated with a different ligand, 2-thenoyltrifluoroacetone (TTA) depicted below. In the solvent extraction literature, synergistic extraction of lanthanides, actinides, and alkaline-earth metals was reported using TTA with organophosphorus esters.[49]



2-thenoyltrifluoroacetone (TTA)

TABLE 6

EUROPIUM EXTRACTION USING SIRs

	pH 1.0		pH 2.0	
resin	% MB	log D	% MB	log D
DE	101	3.41	94	0.89
DE/Cyanex		-0.04[a]		2.33[a]
PS/Cyanex	100	-0.18	100	1.97
PS	102	-0.45	93	-0.69

[a] These distributions were determined from aqueous counts only. The sticky nature of these beads prevented removal of all of the beads from the vial for counting.

Figure 8 illustrates that extraction of europium by the bifunctional DE/TTA system is due to the fixed ligand rather than the free ligand indicated by the good agreement between the DE and DE/TTA trends. It was of concern that metal ion extraction by the diester increased with increasing pH. The anticipated trend is exactly opposite of the observed trend. The resin is behaving like a monoester, and the equilibrium in equation 8 shifts left, towards uncomplexed europium.

$$\underset{\text{resin}}{3\,H^+} + Eu^{3+} + 3\,NO_3^- \rightleftharpoons \underset{\text{resin}}{Eu^{3+}} + 3\,H^+ + 3\,NO_3^- \qquad (8)$$

Further investigation showed that the monoester does exist in the diethylester resin, and under these experimental conditions the impurity was present in large enough quantites to effectively bind all of the metal in the contact vessels.

The DE/Cyanex system was also evaluated for extraction of uranium. The distributions in Table 7 show no no evidence of synergism under these conditions. In fact, there appears to be a slight degree of antagonism at pH 1.0. This is likely due to hydrogen bonding between the phosphoryl oxygen in the diester and the acidic proton of the ligand, as illustrated in Figure 9.

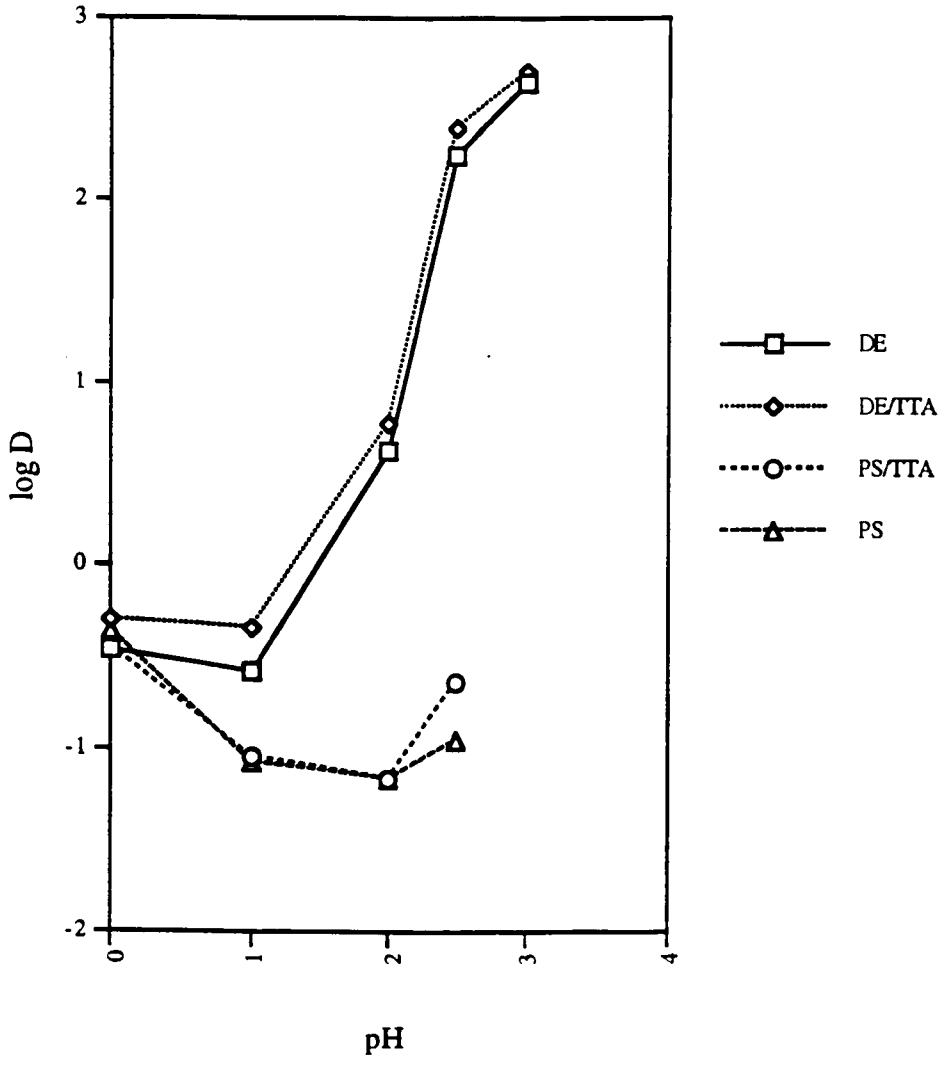
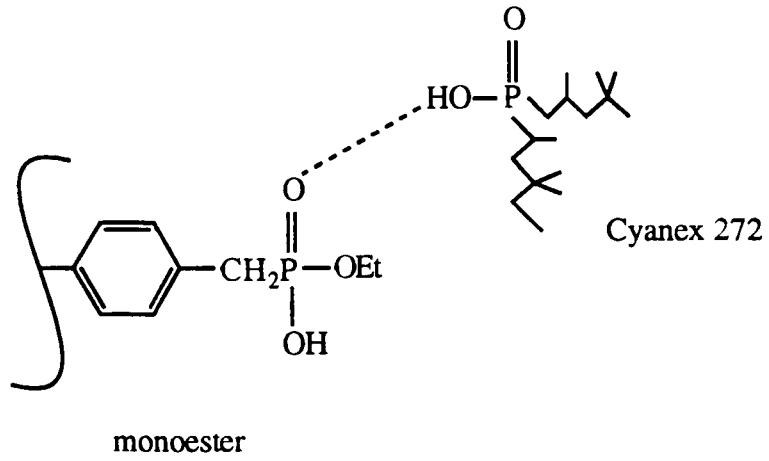


Figure 8. Europium extraction using SIRs. The pH dependence of Eu^{3+} extraction using a diethylester resin impregnated with 2-thenoyltrifluoroacetone.

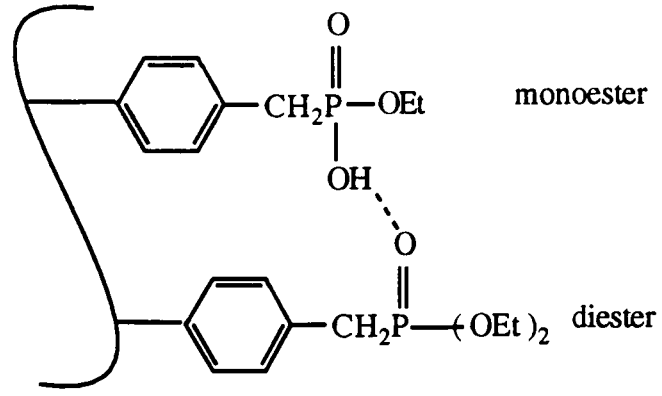
TABLE 7

URANIUM EXTRACTION USING SIRs

sample	log D (pH 1.0)	log D (pH 2.0)
DE	0.85	0.57
DE/Cyanex	0.56	0.78
PS/Cyanex	0.75	0.80
PS	-0.31	-0.30



(a.)



(b.)

Figure 9. Hydrogen bonding between (a) Cyanex 272® and a monoester functionality on the resin bead, and (b) the monoester and diethylester functionalities on the resin bead.

CHAPTER IV

EXTRACTION OF MERCURY USING SULFUR-CONTAINING REAGENTS

INTRODUCTION

Techniques for isolation of mercury in acidic media have been well established.[50,51] Fewer results have been reported, however, for extracting mercury under less acidic or neutral conditions. Some important applications fall in these pH ranges. Removal of mercury from environmental samples often requires operation in the pH range 6-8. It is perhaps more difficult to study extraction at these pHs, because the mercury is hydrolyzed rather than existing in its cationic form.[52]

It is known that the presence of the sulfur atom facilitates extraction of soft metal ions.[53] Accordingly, sulfur-containing extractants such as di-n-hexyl sulfide (DHS) and various thia-macrocycles have been studied extensively.[54-57] In this chapter, results obtained using several pH ranges are presented. Several thia-ligands were examined for extraction of mercury in conjuntion with carboxylic acid beads at pH 6.0, and with phosphonic acid beads in 1.0 M HNO_3. Solvent extraction studies using thia-ligands were done as well, substituting 1,1-heptylmethyl nonanoic acid (HMHN) in place of the carboxylic acid resin beads.

EXPERMENTAL

All SIRs used in this chapter were prepared using the wet impregnation method, detailed in chapter two. The ligands examined in this work include:

di-n-hexyl sulfide (DHS, Aldrich), 1,1-heptylmethyl nonanoic acid (custom synthesized by Aldrich), 3,6-dithiaoctane, 1,4,8,11-tetrathiacyclotetradecane (TT14C4, Aldrich), 3,6,10,13-tetrathiapentadecane (TTPD). These compounds were used without further purification.

All solutions at pH 6.0, unless otherwise designated, were prepared by adding enough acetic acid to produce a concentration of 0.01 M in the final volume. The matrix was also 0.20-M $NaNO_3$. Mercury-containing solutions were all 1.0 x 10^{-4}-N mercury nitrate. Metal partitioning was traced using Hg-203 (New England Nuclear). In some of the solvent-extraction experiments, the Hg-203 was initially added to the organic phase, and equilibrated with an aqueous matrix (containing no metal). When distribution coefficients for samples in which the mercury was initially added to the aqueous phase were similar to those in which the mercury had been added to the organic phase initially, it was concluded that equilibrium had been established. For SIR experiments, it was more practical to do a time-dependence study to determine how long samples must be mixed to reach equilibrium. The point on a log D vs. time plot where the distribution leveled off (with at least one day of measurements made beyond this point) was assumed to be a sufficient length of time.

RESULTS AND DISCUSSION

A partially functionalized phosphonic acid resin (0.890 meq P/g resin, 4.98 meq Cl/g resin) impregnated with DHS, extracted Hg^{2+} from an aqueous 1.0-M HNO_3 solution. Examining the results in Table 8, it can be concluded that the extraction is brought about by the DHS rather than a cooperative effort, since

the PS/DHS control has the same distribution coefficient as the bifunctional system.

TABLE 8

MERCURY EXTRACTION FROM 1.0 M NITRIC ACID

USING PHOSPHONIC ACID BEADS IMPREGNATED WITH DHS

resin	log D
phosphonic acid	0.42
phosphonic acid/DHS	2.23
PS/DHS	2.21
PS	-0.88

The next set of conditons were solutions at pH 6.0, buffered using 0.01-M citric acid/sodium citrate, with 0.20-M $NaNO_3$ present for ionic strength. Results appearing in Table 9 suggest that there is perhaps slight synergism operating in the COOH/DTO system under these conditions. Considering the scatter (the difference between duplicate samples) in the results, perhaps the difference between COOH and COOH/DTO extraction is less apparent. The COOH/DHS system behaves in a similar manner, with no extraction by the mobile ligand alone, reasonable extraction by the acid functionality, and marginal cooperative action in the bifunctional system. Results from the tetrathiapentadecane-impregnate, on the other hand, suggest antagonism is present in the bifunctional system. This is indicated by the greatly diminished distribution coefficient of the COOH/TTPD SIR in comparision with the carboxylic acid bead

TABLE 9

MERCURY EXTRACTION AT pH 6.0 USING COOH BEADS

IMPREGNATED WITH DTO, DHS OR TTPD

resin	log D	log D (duplicate)
COOH	1.34	1.27
COOH/DTO	1.50	1.41
PS/DTO	-0.47	-0.36
PS	-0.54	-------
COOH	1.35	-------
COOH/DHS	1.55	1.48
PS/DHS	-0.50	-0.58
PS	-1.0	-------
COOH	1.35	1.29
COOH/TTPD	0.73	0.68
PS/TTPD	-0.33	-0.43
PS	-0.42	-------

alone. The thia-ligand is known to complex mercury with quite high efficiency in the presence of an ion exchanger and leads one to question whether the ligand may be complexing the mercury in the aqueous phase, rather than in the resin phase.[58] This idea was not confirmed since ligands which leach from the beads are of little use for SIR application. A solvent-extraction experiment using TTPD with a long-chain carboxylic acid, HMHN, was done under conditions identical to those in the SIR experiment. The idea was that the HMHN would mimic the behavior of the carboxylic acid beads, and equilibration would be more rapid. Table 10 shows the extraction trend in the solvent system, which is similar to extraction by the SIR analog. These values, however, are not equilibrium values, as indicated by the difference in distribution of the bifunctional system with mercury initially added to opposite phases. Certainly the numbers will change to some degree as equilibrium is established, however, the trend will most likely remain the same.

To examine the extraction dependence on the acetate anion, citric acid was substituted for the acetic acid during the solution preparation. This experiment was done during a time when the Hg-203 isotope was unavailable, so silver was used rather than mercury. The specific isotope was Ag-110m (New England Nuclear), and beta scintillation spectrometry was the method of analysis. The results appear in Table 11 and indicate that silver complexation by DHS is favored in the citrate media more than in the acetate buffer, because the carboxylic acid distributions are similar, while both DHS-containing resins have higher distributions in the citrate matrix. The citrate anion is prevented

TABLE 10

SOLVENT EXTRACTION OF MERCURY USING HMHN/TTPD AT pH 6.0

resin	log D	log D (duplicate)
HMHN/TTPD	0.85	0.88
HMHN	1.33	1.35
TTPD	-0.63	------
HMHN/TTPD[1]	1.76	1.96

[1] Radiotracer was initially added to the organic phase.

from extraction with the metal because the three hydroxide groups on the molecule render it quite hydrophilic, while the acetate anion can readily go into the polymer. In other words, if the citrate buffer complexes the Ag^+, the complex remains in the aqueous phase. The citrate/Ag^+ stability constant is probably low, explaining higher distribution coefficients in this matrix.

TABLE 11

ANION DEPENDENCE OF MERCURY EXTRACTION

BY COOH/DHS SIRS AT pH 6.0

resin	citrate buffer log D	acetate buffer log D
COOH	1.33	1.35
COOH/DHS	2.04	1.55
PS/DHS	1.06	-0.50
PS	-0.13	-1.0

A solvent extraction experiment was done with a cyclic thia-ligand and HMHN. This was also at pH 6.0 in acetate buffer. Table 12 shows the thia-macrocycle extracts the mercury quite readily by itself but, when in the presence of HMHN, does so less efficiently. Similarly, the HMHN complexes more metal when it is the sole extractant present. It may therefore be said the HMHN/TT14C4 combination interacts antagonistically.

TABLE 12

SOLVENT EXTRACTION OF MERCURY USING HMHN/TT14C4

AT pH 6.0 IN ACETATE BUFFER

extractant	log D
HMHN	1.18
HMHN/TT14C4	1.01
TT14C4	1.39

A comparison mercury extraction by HMHN and DHS in two different solvents was made. Again, the pH 6.0 in citrate buffer matrix was used as the aqueous phase. Liquid extractants were brought up separately in both toluene and hexadecane. The results in Table 13 show the choice between these two solvents makes no difference in extraction.

TABLE 13

SOLVENT DEPENDENCE OF MERCURY EXTRACTION BY HMHN AT pH 6.0

HEXADECANE = HD, TOL = TOLUENE

ligand/solvent	log D	log D (duplicate)
HMHN/TOL	1.12	1.13
HMHN/HD	1.12	1.11
DHS/TOL	-1.49	-1.52
DHS/HD	-1.29	-1.31

CHAPTER V

METAL ION COMPLEXATION USING BIFUNCTIONAL INTERPENETRATING POLYMER NETWORKS

INTRODUCTION

Interpenetrating polymer networks (IPNs) are a novel class of materials which have been studied for numerous applications.[59] An IPN is defined as a combination of two or more polymers, at least one of which is synthesized in the presence of the other.[60] Bifunctional IPNs offer unique advantages in substrate recognition because the ligand-containing chain segments are not covalently bound to the polymer backbone, allowing greater versatility in the preparative scheme.

Considerable interest has surfaced in recent years in the development and use of polymeric reagents for metal-ion recovery from waste streams and environmental samples.[61,62] Other applications include removal of toxic metal ions from bath liquors and solution purification.[63,64] The polymer matrix often offers advantages over solvent-extraction techniques such as elimination of incomplete phase separation and reduction of losses through entrainment. Bifunctional polymers and solvent-impregnated resins can provide unique selectivities while maintaining the above mentioned characteristics.[65,66] The polymers used in this work include monofunctional vinylpyridine and acrylic acid IPNs; and one IPN containing both ligands in a 50:50 ratio. The synthesis, which has been reported previously,[67] involves a primary polymer, polystyrene beads 2.0 % crosslinked with divinylbenzene

(DVB), into which vinylpyridine, ethyl acrylate, or both, along with an initiator and 10.0 % DVB are incorporated by swelling in an appropriate solvent. Polymerization produces the second polymer which is entangled within the polystyrene.

EXPERIMENTAL

Reagents and sample preparation

Aqueous metal-ion solutions were prepared by dissolving the nitrate salts in enough glacial acetic acid (analytical grade, Mallinckrodt) to produce a concentration of 0.60 N in the final volume. A radiotracer was added and diluted to 80 % of the total volume with nanopure deionized water. A calibrated semi-micro combination pH electrode (Corning) was used to continuously monitor the pH while adding 50 % NaOH (reagent grade, J. T. Baker Chemical Co.) until a final pH of 4.9 was obtained. The electrode was rinsed into the beaker, and the beaker contents were quantitatively transferred to a volumetric flask. Cadmium nitrate tetrahydrate (99.4 %, J. T. Baker Chemical Co.), zinc nitrate hexahydrate (99.6 %, J. T. Baker Chemical Co.), cobalt nitrate hexahydrate (99.102 %, E. M. Science, Gibbstown, N.J.), cupric nitrate pentahemi-hydrate (reagent grade, E. M. Science), nickel nitrate hexahydrate (99.87 %, Fisher Scientific Co.), mercury nitrate monohydrate (99.0 %, MCB Manufacturing Chemists, Inc., Cincinnati, OH), and europium(lll) nitrate hexahydrate (99.99 %, Aldrich) were used without further purification. Radioisotopes Eu-152/154 (Oak Ridge National Laboratory, Oak Ridge, TN), Hg-203, Zn-65, Co-60, Ni-63, and Cd-109 (New England Nuclear, Billerica, MA) were obtained either in the nitrate or chloride form. Metal chlorides were

metathesized by slowly heating an aliquot in a petri dish to dryness, followed by addition of 0.999-N HNO_3 (reagent grade, J. T. Baker Chemical Co.) three times before quantitatively transferring the residue to a volumetric flask and diluting with 0.10-N HNO_3.

Metal ion experiments

Buchner-dry resins were pre-equilibrated with the matrix by slowly rotating vials on a rugged rotator (Glas-Col Apparatus Co., Terre Haute, IN) for one hour, removing the solution four times (every 15 minutes) and replacing with fresh solution. Enough resin to produce one milliequivalent of ligand sites was placed into 4.0-mL plastic scintillation vials with 3.0 mL of 1.0×10^{-4}-N metal nitrate solution. The vials were mounted onto a metal disk and rotated at 26 rpm. Following equilibration, the aqueous phase was sampled and assayed by scintillation spectrometry. In the experiments using gamma tracers, the resins were also counted by pouring the IPNs into clean vials, removing the aqueous phase, and rapidly rinsing twice with deionized water prior to counting. Separation of liquid from the beads was accomplished by inserting a glass wool plug atop the beads, then quickly removing the liquid by suction using the apparatus illustrated in Figure 3. The plastic straw tip was replaced between samples to prevent cross-contamination. Polystyrene beads were treated identically to the IPNs and analyzed in all experiments as an additional control.

Competitive metal ion experiment

Resins were treated in the same manner as described above except 10.0 mL of a metal-ion solution containing 5.0×10^{-5}-N $Cu(NO_3)_2$, 5.0×10^{-5}-N $Co(NO_3)_2$, and

5.0×10^{-5}-N $Zn(NO_3)_2$ was contacted with enough resin to deliver 1 mequiv of ligand sites. Samples were equilibrated for one week, after which the aqueous phase was removed and analyzed by AA. All standard solutions for calibration contained equivalent amounts of all three metals.

Instrumentation

Gamma-emitting isotopes were counted with a NaI well-type spectrometer, and beta-emitters were mixed with Ultima Gold scintillation cocktail (Packard, Meriden, CT) and counted on a TRI-CARB liquid scintillation spectrometer. In most cases, 10,000 counts above background were obtained to produce a statistical counting error of ≤ 1 %. When it was impractical to achieve these counting statistics, the mass balance was used to determine reliability of the data. Data having mass balances less than 98% or greater than 102 % were rejected.

FTIR spectra (Figure 10) were acquired using a BIO-RAD FTS-60 Spectrometer (Bio-Rad Laboratories, Inc., Cambridge, MA). Water was removed from resins by contacting Buchner-dry beads twice with methanol and four times with acetone. Resins were then vacuum dried (25 ^{o}C, 5 mm Hg) for 12 hours. Dry IPNs were ground with a mortar and pestle and pressed into KBr pellets.

The copper samples were analyzed by atomic absorption spectroscopy rather than using tracer techniques due to the very short half-lives of available copper isotopes. The measurements were made using a Varian spectrometer operated in the absorption mode.

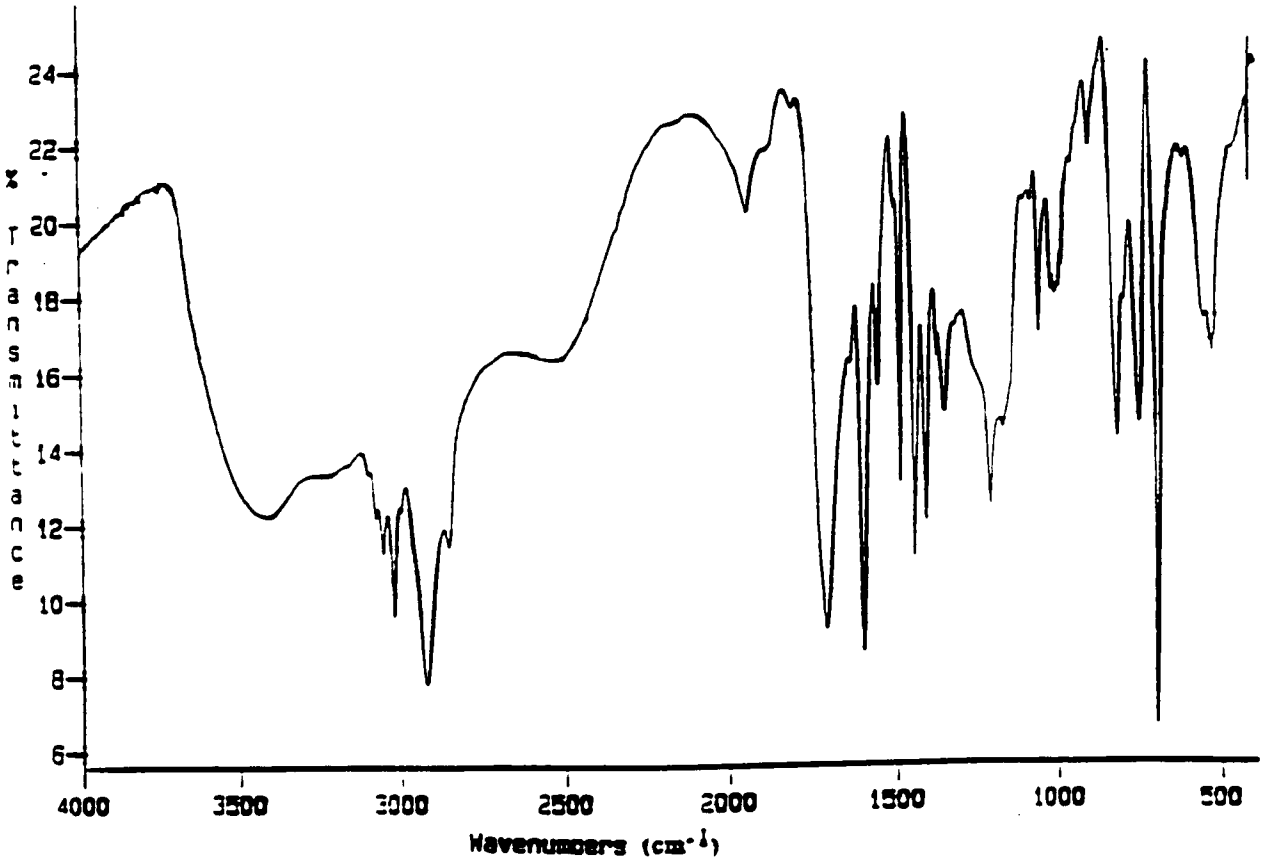


Figure 10. FTIR spectrum of the vinylpyridine/acrylic acid IPN pressed in a KBr pellet.

Mixed bed experiment

This type of experiment may be used to illustrate synergistic binding of metal ions. Enough bifunctional vinylpyridine/acrylic acid polymer to produce 1 mequiv (sum total of acid and base sites in sample) of ligand sites is weighed into a vial. In a separate vial, enough monofunctional polymer is introduced to produce 0.5 mequiv of acid and 0.5 mequiv of base sites. The physical barrier of the polymer matrix in the mixed bed prevents ligand interaction so by examining differences in metal-ion distributions in these two samples, one may learn if ligand cooperation is indicated. All samples were prepared and analyzed in duplicate.

RESULTS AND DISCUSSION

Synergism has been defined as the cooperative action of different ligands in producing an effect greater than the sum of the effects of all ligands acting separately.[68] Many reports of synergism have appeared in the solvent-extraction literature.[69-73] In the current experiments, metal-ion extraction via a synergistic ligand interaction was explored by comparing extraction by the bifunctional acrylate/pyridine IPN with that exhibited by monofunctional acrylic acid and vinylpyridine IPNs. An estimation of the synergistic effect in solvent-extraction systems has been defined as the synergistic coefficient (s.c.) and is calculated using equation (9).[74]

$$\text{s.c.} = \frac{D_{\text{bifunctional}}}{D_{\text{monofunctional 1}} + D_{\text{monofunctional 2}}} \qquad (9)$$

Application of this value may be extended to polymeric extraction systems at low metal loading. The s.c. is most useful when accompanied by additional information including percent extracted and individual distribution coefficients. Inclusion of this additional information is of increasing importance in systems in which all or almost all of the metal ion is incorporated by the polymers. When the extraction is high, the error in the aqueous phase counts is also high. Such experimental difficulties are passed on to the s.c., until at 100 % extraction, the s.c. can no longer be calculated, because the distribution coefficient is undefinable, as illustrated in equation 10.

$$D = \frac{c_{org}}{c_{aq}} = \frac{c_{org}\ (a\ number)}{0} = \text{undefined} \qquad (10)$$

Table 14 shows that the acrylic acid IPN extracts Eu^{3+} with high efficiency; however, when in the presence of the vinylpyridine ligand, the amount of metal extracted decreases by nearly a factor of 2. Although an excess of acid sites are present (0.5 mequiv in the bifunctional sample and 10^{-4} mequiv of metal), much of the metal remains in the aqueous phase, suggesting that an interaction such as hydrogen bonding plays an important role in the observed antagonism. This was further investigated by analyzing the IPNs by FTIR. The peaks occurring at 1950 cm^{-1} and 2530 cm^{-1} in Figure 10 are indicative of hydrogen bonding between the two ligands.[75] Apparently the affinity of the hard metals for the ligands in the bifunctional IPN was not strong enough to overcome this force and hence, more metal was complexed by the acid resin alone. At pH 5, the pyridine (pKb 8.75) is mostly in the protonated form, and

TABLE 14

EUROPIUM EXTRACTION USING IPNs

resin	metal	log D	% extr.	s.c.
VP	Eu^{3+}	0.48	35	
AA	Eu^{3+}	3.31	100	
bif	Eu^{3+}	1.34	79	0.012

Table 14. Results from experiments with hard Lewis acid metals. VP corresponds to the monofunctional vinylpyridine IPN, AA corresponds to the acrylic acid IPN, and bif to the bifunctional IPN. Percent extracted is abbreviated, % extr.

the acrylic acid (pKa 4.25) exists both in its protonated form and as carboxylate anion. The weak absorption bands at 1400 cm^{-1} and 1600 cm^{-1} in Figure 9 represent asymmetric and symmetric carboxylate stretches respectively, indicating a small fraction of deprotonated acid.

Table 15 illustrates efficient binding of transition metal ions by the bifunctional IPN. The acid IPN extracts all metals except Co^{2+} almost as well as the bifunctional polymer, while only Ni^{2+} and Cu^{2+} have a strong affinity for the vinylpyridine IPN. The synergistic extraction of Co^{2+}, Ni^{2+} and Zn^{2+} is shown in Table 15. To provide further support that the two ligands in the bifunctional IPN do indeed work together to complex the metal, an addititional experiment was necessary. Synergism was further confirmed by performing a mixed-bed analysis. The mixed-bed distributions in Table 16 are intermediate between the monofunctional metal ion distributions and substantially lower than those with the bifunctional IPN, indicating extraction enhancement by the combination of ligands.

Table 17 contains results from IPN contact studies with some soft metals. All three polymers complexed the mercury with high efficiency, producing an indeterminate s.c. Extraction of cadmium was achieved by the acid ligand, and no synergism occured in the bifunctional beads, which is reflected in the very good agreement between log D values of the acid and bifunctional resins. On the basis of the hard/soft acid/base classification system,[76] one would not predict strong bonding of soft metals by a pyridine ligand, which is a borderline Lewis base. To better understand synergistic binding of metals, other factors must be considered such as other ligands present in the aqueous

TABLE 15

TRANSITION METAL ION EXTRACTION USING IPNs

resin	metal ion	log D	% extr.	s.c.
VP	Ni^{2+}	2.02	95	
AA	Ni^{2+}	2.11	96	
bif	Ni^{2+}	2.77	99	2.5
VP	Co^{2+}	0.58	35	
AA	Co^{2+}	1.44	82	
bif	Co^{2+}	1.90	93	2.7
VP	Zn^{2+}	0.76	51	
AA	Zn^{2+}	1.88	93	
bif	Zn^{2+}	2.04	95	1.3
VP	Cu^{2+}	3.75_{max}	99	
AA	Cu^{2+}	3.75_{max}	99	
bif	Cu^{2+}	3.75_{max}	99	

Table 15. Results from experiments with borderline Lewis acid metal ions.

TABLE 16

DETERMINATION OF COOPERATIVE LIGAND ACTION

TO COMPLEX METAL CATION

resin	metal ion	log D
bif	Zn^{2+}	2.19
bif	"	2.27
VP	"	0.77
VP	"	0.76
AA	"	1.82
AA	"	1.81
VP/AA (mixed-bed)	"	1.76
VP/AA (mixed-bed)	"	1.72

Table 16. Mixed-bed study results. VP corresponds to 1 mequiv of monofunctional vinylpyridine IPN, AA corresponds to 1 mequiv of acrylic acid IPN, bif to the bifunctional IPN sample containing 0.5 mequiv of both acid and base ligands, and VP/AA corresponds to the mixed bed samples which include 0.5 mequiv of each of the monofunctional IPNs.

TABLE 17

SOFT METAL ION EXTRACTION

resin	metal ion	log D	% extr.	s.c.
VP	Hg^{2+}	2.49	98	
AA	"	2.60	99	
bif	"	2.62	99	0.46
VP	Cd^{2+}	0.98	37	
AA	"	3.37	99	
bif	"	3.38	99	1.03

Table 17. VP corresponds to the vinylpyridine IPN, AA to the acrylic acid IPN, bif to the bifunctional IPN.

matrix and their relative affinities for the metal of interest. This interaction may be illustrated using equilibrium constants (equation 11).

$$M^{2+} + 2\,H_2O \rightleftharpoons M(OH)_2 + 2H^+$$

$$K = \frac{\left(M(OH)_2\right)(H^+)^2}{\left(M^{2+}\right)\left(H_2O\right)^2} \qquad (11)$$

A low value of the logarithm of the equilibrium constant (log K) indicates a shift to the left in the equilibrium expression. Low values of log K were found in the literature for metals which were synergistically extracted by the bifunctional system.[77] The most favorable extraction conditions are at a pH where the ligand operates appropriately, but also where the metal is in its cationic form. Metals which are hydrolyzed and tightly bind OH^- are much more hydrophilic than other metal ions, and less likely to transfer to an organic phase. Metal/acetate complexes; however, are readily extracted because the acetate groups are less hydrophilic and may be extracted into the organic phase along with the metal. To support this theory, an additional experiment was done using 0.60 M citric acid/citrate buffer instead of acetate. Cobalt (Co^{2+}) was the metal ion selected for the experiment because it has a smaller log K value with citrate than with acetate. Table 18 illustrates the importance of the matrix of the aqueous phase. Very low distributions were obtained for all three IPNs in a matrix containing the citrate anion. This could be due to formation of a very stable and hydrophilic metal/hydroxide complex, preventing interaction between the ligands in the polymer and the cobalt.

TABLE 18

COBALT ION EXTRACTION FROM CITRATE BUFFER MATRIX

resin	metal ion	log D
bif	Co^{2+}	-0.30
bif	"	-0.31
VP	"	-0.76
VP	"	-0.79
AA	"	-0.54
AA	"	-0.57
PS	"	-0.53

Table 18. VP corresponds to the vinylpyridine IPN, AA to the acrylic acid IPN, bif to the bifunctional IPN and PS to polystyrene.

A competitive metal ion study was done to observe if the synergism operates when a several metals are present in the aqueous phase together, and to determine if the IPNs exhibit any selectivity among the few transition metals which were examined. Table 19 shows that the synergism is preserved in the bifunctional system for Zn^{2+}, Cu^{2+}, and Co^{2+}. The loading trend in the acrylic acid IPN is $Cu^{2+} > Co^{2+} > Zn^{2+}$. In the bifunctional and vinylpyridine IPNs, the trend is $Cu^{2+} > Zn^{2+} > Co^{2+}$.

In summary, the bifunctional vinylpyridine/acrylic acid IPN extracts various transition metals from dilute solutions with high efficiency. The extraction enhancement in the bifunctional IPN can be quantified as the synergistic coefficient. The metal-ion extraction trend by the vinylpyridine/acrylic acid IPN, determined using percent extracted data, is $Cu^{2+} = Cd^{2+} > Ni^{2+} = Hg^{2+} > Zn^{2+} > Co^{2+} >> Eu^{3+}$.

Based on the experiments with these selected metal cations, some conclusions may be drawn to investigate further. The synergistic systems in these studies have at least two features in common. First, on the basis of hard/soft Lewis acid/base chemistry, each metal ion cooperatively bound is a borderline-to-soft Lewis metal, which is a likely candidate for complexation with pyridine. Second, the operative pH is one at which the metal ion is likely to occur as a cation rather than a metal hydroxide. This appears to be of primary importance when considering factors influencing synergistic binding of metal ions. The most favorable conditions occur when the metal has an affinity for one of the ligands, strong enough to overcome the intermolecular hydrogen bonding in the polymer, and the metal is cationic or associated with

TABLE 19

COMPETITIVE METAL ION STUDY

sample	metal ion	final conc. (N)	% absorb.	log D
bif	Cu^{2+}	7.60×10^{-7}	98	1.56
bif	"	1.79×10^{-7}	99	2.20
VP	"	2.50×10^{-6}	95	1.02
VP	"	1.92×10^{-6}	96	1.14
AA	"	6.57×10^{-6}	87	0.56
AA	"	5.99×10^{-6}	88	0.61
PS	"	4.89×10^{-5}	2.0	-1.79
bif	Zn^{2+}	5.03×10^{-6}	90	0.70
bif	"	3.87×10^{-6}	92	0.83
VP	"	3.69×10^{-5}	26	-0.70
VP	"	3.44×10^{-5}	31	-0.60
AA	"	2.72×10^{-5}	45	-0.34
AA	"	2.47×10^{-5}	51	-0.25
PS	"	4.87×10^{-5}	2.6	-1.69
bif	Co^{2+}	1.56×10^{-5}	69	0.10
bif	"	1.61×10^{-5}	68	0.08
VP	"	4.36×10^{-5}	13	-1.09
VP	"	4.17×10^{-5}	16	-0.96
AA	"	2.18×10^{-5}	56	-0.15
AA	"	2.09×10^{-5}	58	-0.11
PS	"	4.88×10^{-5}	2.3	-1.75

anion(s) organophilic enough to be extracted along with the metal. In the design of synergistic extraction systems, several factors must be considered including: hard/soft acid/base interactions, matrix effects, pH, and stability constants of the aqueous species present with the metal ions.

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