

UNIVERSITY HONORS PROGRAM

SENIOR PROJECT - APPROVAL

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PROJECT TITLE: Synthesis and Characterization of

Sulfonated β -Ketophosphonate Ion Exchange Resins

I have reviewed this completed senior honors thesis with this student and certify that it is a project commensurate with honors level undergraduate research in this field.

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Date: Dec 10, 1997

Comments (Optional):

This is a particularly strong thesis which shows a good understanding of the introductory material, the experimental technique, and the results obtained in the laboratory.

Synthesis and Characterization of
Sulfonated β -Ketophosphonate Ion Exchange Resins

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Abstract

Ion exchange resins were first used in the 1930's. Since then, they have increased in durability and versatility. Many ion exchange resins are now used commercially for the separation, purification, and concentration of targeted species in such fields as food processing, water remediation, and catalysis.

Sulfonated β -ketophosphonate ion exchange resins were prepared and characterized. These resins were compared to the β -ketophosphonic acid, phosphonic acid, and sulfonated phosphonic acid ion exchange resins as controls. The ability of these resins to complex europium(III), copper (II), and lead(II) was tested with metal ion studies with durations of $\frac{1}{2}$ hr and 24 hrs for each metal. When the resins were compared, the sulfonated resins exhibited a higher tendency to complex the metal ions than the non-sulfonated resins. This tendency was the most significant in the complexation of europium(III); the sulfonated β -ketophosphonic acid resin was the most efficient of the resins in extracting this metal.

Introduction

Polymers are uniquely versatile substances made up of long chains of atoms which provide many of the material comforts we have today. Many chemists did not accept the existence of such large, stable molecules until about the 1920's. The use of polymers as fibers, plastics, adhesives, and resins increased dramatically after WWII due to their strength, elasticity, and corrosion resistance.¹

Ion exchange resins were introduced in the 1930's.² Though their first use was for the softening and demineralization of water for industrial needs, their range of application has broadened in the last 60 years³ due to their physical and chemical improvements.² The original usage of ion exchange resins for the purification of water continues today as their largest application⁴ in industries such as nuclear waste water remediation.³ These resins are used world wide; for example, they are used in Scandinavia for water purification and also in Hannover for the removal of humic acids from water sources.⁵ Ion exchange resins are also used in hydrometallurgy to extract metals from ores,⁴ in the chemical industry to produce pure solvents and chemicals, and as catalysts for various chemical reactions.³ In biochemistry, polymer supported reagents are used for the synthesis of peptides, oligosaccharides, and oligonucleotides. They even incorporate enzymes which act as biological catalysts.⁴

Ion exchange resins can be used to concentrate small amounts of the target material from large volumes of solution to smaller volumes. An example of this type of usage is the concentration of vitamins and antibodies from fermentation broths. For example, streptomycin is extracted with a weak acid cation exchanger, and penicillin is extracted with an anion exchange resin. Ion exchange resins are used in the pharmaceutical industry to provide a controlled release of drugs to the patients; they are similarly used in hydroculture to provide nutrients to plants.⁶ In the semiconductor industry, 2- propanol is used as a solvent to remove any remaining water off the surface of the semiconductor wafers after they are produced. The 2-propanol is recycled and purified with ion exchange resins so that it is free of any metals before it is reused.⁷ Ion exchange resins are also used in food processing to remove unwanted colors and minerals from the products. Some foods that are treated with the resins include glycerine, gelatine,

alcohols, fruit juices, sugars, whey, and wine. The use of ion exchange resins in the sugar industry is very important; an example is for the purification of fructose used by soda manufacturers.⁶

The earliest method for the purification of water was the use of sand;⁸ now, ion exchange resins are used for the production of high quality water. These resins are used in nuclear power plants³ to remove ionic and solid impurities from the water.⁹ This is an important use for the resins because of the scale and corrosion that may affect the water supply within the plants and also due to the variety of sources for water with their particular contaminants. The water may be drawn from wells, rivers, lakes, or municipal sources and can contain different amounts of dissolved or suspended materials dependent on the location and season.³ There is also an increase in interest for the recycling of water due to low supplies of water in some areas of the world and because of the increase in treatment and disposal costs;¹⁰ it is estimated that an average plant uses over a million gallons of water per year.¹¹ The water used in nuclear power stations must limit the amounts of chlorides, sulfates, and sodium to sub-parts per billion levels for use in supercritical boilers which produce steam.⁶ Clean water is also necessary for human consumption. Over 500 public water supply systems exceed EPA limits for contaminants in the United States. A test of an ion exchange process to remove radium from well-water is currently in progress in Lemont, IL.¹² In McFarland, CA, an ion exchange plant has been built to remove the nitrates from the city's water supply; the presence of these nitrates is due to the use of nitrogen fertilizers in the area.¹³

There is also a need for the purification of water after it has been used for industrial processes. The treatment of radioactive wastes is an important example; the ion exchange resins are used to remove toxic ions from water that is to be returned to the surrounding environment. Usually the radioactive ions are present in highly acidic solutions and are mixed with large amounts of dissolved solids and other organic compounds. Some environmentally benign ions such as Na(I), K(I), and Ca(II) are also present in higher concentrations than the radioactive ions such as Pb(II) and Hg(II).⁸ The need for separation of this mixture makes remediation of the waste water chemically and economically challenging.¹⁴ The ion exchange resins produced 50 years ago were too weak to be used with radioactive materials, and also the exchange kinetics of the resins

were too slow. Improved ion exchange resins are now being used to extract metals such as uranium, plutonium,¹⁵ ruthenium, and technetium from waste water. The resins are encased in an inorganic material which is stronger against the effects of radiation than the previous resins. The matrix also insures that the resins are not washed into the output stream of water. The removal of these wastes is especially important to protect the aquatic life of the rivers and seas which serve as the outlets for many industrial plants.¹⁶

The ion exchange resins which are commercially available today are about ½ mm in diameter; they are usually copolymers of styrene and divinylbenzene or acrylic acid.¹⁰ They are available as macroporous or gel resins and are very durable. The development of processes such as continuous operation and counterflow regeneration have increased the long term efficiency of the resins which in turn decreases the amount of solvent needed to regenerate the resins. Due to these advantages, markets for ion exchange resins are continuously growing; examples include industries such as food processing and specialty applications (5 to 8 % increase yearly), demineralization (2 to 5 % yearly), and in mining (0.5 % yearly).¹⁷

Some alternatives to the use of ion exchange resins are electrodialysis, reverse osmosis, and electrodeionization.³ Precipitation of wastes as alkaline sludge is also another method of waste treatment. The difficulties with this method include the high cost of the equipment, the space needed, and its sensitivity to temperature.¹⁸ Another method of waste remediation is the use of solvent extraction techniques. This method is versatile, has a rapid rate of extraction, and can be very selective. The metal ions in the aqueous phase (the wastewater) are contacted with an organic solvent which extracts the metals. The solvent is then contacted with fresh aqueous solvent to remove the metal ions; this produces a concentrated solution.⁴ This method is used to remove ions such as copper from solutions produced during mining processes.¹⁹

Solvent extraction requires the use of a large amount of inflammable solvent and, like the alkaline sludge method, requires a large amount of space. Due to these requirements, solvent extraction is not economically efficient for large volumes of dilute solutions.¹⁹ The organic solvent used may also be lost to the environment through evaporation²⁰ or may leach into the aqueous phase which is subsequently released from

the industrial plant. This increases the cost of operation and also raises the toxicity of the water that is returned to the surroundings.¹⁴

The benefits in the use of ion exchange resins over the solvent exchange method stem mainly from the covalently bonded nature of the ligands which extract the ions from the waste water. The ligands chosen for incorporation into the resins are those which perform well under solvent extraction techniques. However, because the ligands are bonded to the resin, there is very little loss of ligand to the aqueous phase.¹⁴ An example of a solvent extraction method is PUREX. The advantages of the use of ion exchange resins over PUREX include the compact size of the process, the smaller volume of organic waste created, the ability for the separation of metal ions from each other during reprocessing, and the facile isolation of the resins from the solvent.¹⁵ All ion exchange resins have these advantages; they also have the ability to treat very dilute solutions and can be used in continuous processes.²¹ Some disadvantages of ion exchange resins as compared to other methods of remediation are their lower selectivity for the ions and slower extraction rates.⁴ The rates at which these resins extract the metal ions from waste water may be increased however by increasing the porosity of the resin, decreasing the bead size, or decreasing the amount of crosslinking in the resin.²⁰

An important issue in the use of ion exchange resins is the process of regeneration. Also, if regeneration is not a feasible method for the resin, the methods for disposal of the spent resins must be considered. Regeneration involves three basic steps: first, the bed of resins must be back-washed to remove any accumulated particulate wastes; then the resin must be contacted with a regenerant solvent (for example, a cationic resin should be rinsed with a strongly acidic solution); and finally, the resin must be washed with water. The ion exchange resins are useful because of their ability to bind strongly to the metal ions; this ability must be counteracted in the regeneration process which displaces the metal ions with the original ions of the resin. As a result, ion exchange resins are normally not returned to their original capacities.¹⁰ Regeneration is also dependent on the concentration of the regenerant solvent, the temperature, and the rate of flow of the solvent.³ In some cases, a more selective ion exchange resin may need a stronger regenerant such as a solution of EDTA to remove the metal ions from the ligands in the resin.¹⁴

Regeneration may not be effective for the resins which bind their metals tightly. In this case, these resins must be disposed of as solid waste. Due to the costs and space required for disposal, the mass of the waste should be reduced as much as possible.¹¹ Some decomposition techniques include pyrolysis, incineration, and wet oxidation. Pyrolysis reduces the volume of wastes and also stabilizes them by solidification into cement as a final waste product. Pyrolysis involves temperatures of about 500° C which are lower than those required for incineration.⁹

The overall performance of the ion exchange resins is measured by three factors: the operating capacity, the regenerant dose, and the leakage. The operating capacity is the amount of targeted material the resin can extract from the water during an operating cycle. The regenerant dose is the amount of solvent which is required for the resin to be returned to its intended capacity. The leakage is the amount of targeted material that is not entrapped by the resins and flows from the packed bed. These factors are dependent on the rate of extraction of the metals, the degree of selectivity, and the size of the resin. The amount of crosslinking in the resin and the porosity of the resin (gel type versus macroporous type) may be varied to change the kinetic rate of extraction.¹⁰ The cost of the process is reduced by an increased selectivity of the resin because they will last longer and require fewer regeneration cycles. The costs due to environmental regulations also decreases with an increase in selectivity.¹⁸

The ion exchange resins used in industrial processes must be very strong to withstand the high pressure flow of the solutions through the column any swelling and shrinking due to the slight changes in acidity of the solution that may occur.^{22,15} Some resins are currently available only for laboratory research purposes due to their fragility.¹⁵ Current research on ion exchange resins is flourishing. New methods of synthesis are being explored to improve the selectivity and composition of the resins. Resins are being developed with an increased uniformity which includes characteristics such as composition and size. An increase in uniformity will allow the resins to reach the saturation point at the same time which will extend the resin life by lessening the number regenerant cycles and thus, the amount of regenerant solvent required.¹⁷

The bulk of the ion exchange resin is the polymeric backbone. Polystyrene is commonly used due to its versatility as a reactant and its stability. Another common

polymer used for nucleophilic reactions is poly(vinyl benzyl chloride) which is a chloromethylene derivative of polystyrene. The resins are stabilized by various amounts of crosslinking²³ which is the covalent bridging of the polymer chains; this prevents the resin from dissolving.

The polymeric support itself does not in itself extract the metal ions from solution. The key to selective extraction is the ligand which is introduced to the macromolecular structure by means of chemical reactions. The ligands, which are covalently bound to the support, attract the metals into the resin and hold them within the structure. Ionic ligands are able to attract the metals by exchanging them in the solution with their own cation or anion (for acidic resins, a metal may displace an H^+ for example). Chelating resins have ligands that complex with the metal and thus removes them from solution.¹⁴ Other ligands may operate by redox mechanisms; these may incorporate metal ions that have the ability to oxidize the target species or have organic structures which can reduce the target species.²⁴

Ion exchange resins include cationic and anionic ligands which bind metals through electrostatic attractions. These ionic groups enhance the hydrophilicity of the resin which increases the ability of the metal ions to enter the resin. This increase in accessibility creates a high capacity resin.²³ A common ion exchange resin incorporates the sulfonic acid group. This resin is used for water softening systems and removes metals such as iron, manganese, calcium, and magnesium from water.¹⁴ The sulfonic acid resins have a high capacity for metal ions in acidic solutions due to its own high acidity. However, these resins are not selective in the extraction of metals and can only be used for general purposes when all metal ions need to be removed.²³ Selectivity of the resins is an important requirement; if a particular target species is present in low concentrations with other ions of higher concentration, the effectiveness of the resin will be decreased as it is loaded with unwanted ions. A more selective ligand is the carboxylic acid ligand. The carboxylic acid ligand may only be used with certain solutions because of the ligand's relatively low acidity. If the solution is too acidic, the carboxylic acid ligand will remain protonated and will not ion exchange with the metal ions in solution.⁴ Some resins which have intermediate acidity are the phosphonic acid

resins; these are more selective than the sulfonic acid resins but have a greater ability to extract metal ions from acidic solutions than the carboxylic acid ligands.²⁴

A disadvantage of some ion exchange resins is their poor selectivity of metal ions of the same charge. This is due to the similar free energies of the ion exchange reaction that the metals have with the ligand.²¹ This limitation was addressed by the advent of the dual mechanism bifunctional polymers (DMBPs). These special polymers include two ligands to selectively extract metal ions from solution. The first ligand uses an aspecific mechanism to create a hydrophilic environment for the metal ions. This encourages the ions to enter the hydrophobic resin. The metal ions are selectively trapped by a ligand which is more specific than the first ligand. This mechanism is termed the recognition mechanism. These two ligands work together to increase the capacity of the resin.²⁵

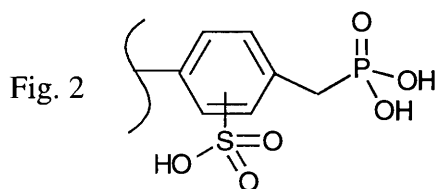
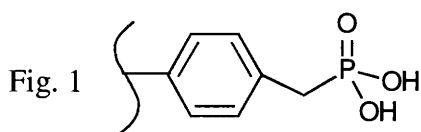
Three types of DMBPs exist; they all have ion exchange as their access mechanism but differ in their recognition mechanisms.²⁵ A common ligand used for the ion exchange mechanism is the sulfonic acid group.¹⁸ Class I DMBPs use a redox reaction as its recognition mechanism. These resins allow for the recovery of the metal in its neutral form. Class II resins use a coordination mechanism to bind the metal ions. The degrees of coordination depend on the acidity or basicity of the metal ion as compared to the ligand in terms of the hard/ soft theory of acids and bases.²⁵ An example of a ligand used for this mechanism is the phosphonic acid group. The Lewis basicity of the phosphoryl oxygen can be altered with its degree of esterification.²³ The third type of DMBPs is the Class III resin which uses a precipitation reaction as its recognition mechanism. This resin creates insoluble metal salts when contacted with a metal ion solution.²⁵

These DMBPs offer many advantages when compared to traditional ion exchange resins. The high rate of extraction of the metals allows for the use of a smaller resin bed and a higher flow rate of solution through the bed. This is economically advantageous because of the lower equipment and total resin costs. These resins can also be used with the existing ion-exchange equipment so a change in the resin type does not necessitate a change in apparatus. These resins may also be regenerated with the same solvents as the traditional resins. One commercially available DMBP resin is the Diphonix resin. Diphonix has the ability to selectively complex zinc, cesium, and magnesium.¹⁸

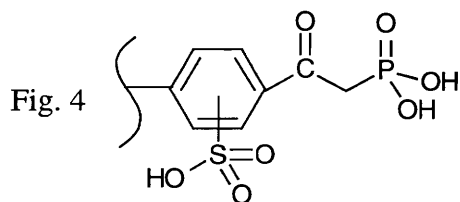
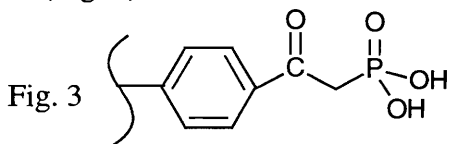
The development of ion exchange resins for industrial uses will become more and more important as the earth's supply of natural resources becomes depleted, and pollution of the environment increases. The strength and durability of the ion exchange resins as well as their versatility seem to promise a growing field of application.

The Synthesis and Characterization of Sulfonated β -Ketophosphonate Ion Exchange Resins

This project involves the synthesis of a Class II DMBP resin with a sulfonic acid group to serve as the access mechanism and a β -ketophosphonic acid group to serve as the recognition mechanism. These new resins are compared to the phosphonic acid resins (Fig. 1) and the sulfonated phosphonic acid resins (Fig. 2) which have been previously studied.



The β -ketophosphonic acid group is expected to coordinate the metal ions more tightly than the phosphonic group alone. The sulfonated β -ketophosphonic acid resins (Fig. 4) are predicted to have faster kinetics and higher capacities than the β -ketophosphonic acid resins (Fig. 3).



These resins were prepared and compared through metal ion studies with europium(III), lead(II), and copper(II). Contact times of 1/2 hr and 24 hrs were used to study the kinetic effects of the sulfonic acid ligand

Experimental Methods

Polystyrene and poly(vinyl benzyl chloride) gel resins crosslinked with 2 % divinyl benzene were prepared by free radical suspension polymerization. The poly(vinyl benzyl chloride) resins were phosphorylated by the Arbusov reaction then hydrolyzed to produce phosphonic acid resins. These resins were then chlorosulfonated to produce sulfonated phosphonic acid resins. These resins were used as controls for comparison to the β -ketophosphonic acid resins and the sulfonated β -ketophosphonic acid resins. The β -ketophosphonic acid resin was prepared by a Friedel-Crafts reaction of bromoacetyl bromide on the polystyrene resin followed by the Perkow reaction and hydrolysis. These resins were then sulfonated via the chlorosulfonation reaction to produce the sulfonated β -ketophosphonic acid resins.

The acid and phosphorous capacities were determined for the resins. The percent solid of the resins was also determined. Metal ion studies on the resins with europium(III), lead(II), and copper(II) were performed for ½ hr and 24 hour contact times.

Free Radical Suspension Polymerization

Free radical suspension polymerization was used to prepare polystyrene and poly(vinyl benzyl chloride) gel resins crosslinked with 2 % divinyl benzene. First, for the poly(vinyl benzyl chloride) gel resins, an organic phase consisting of 286.26 g of vinyl benzyl chloride, 10.90 g divinyl benzene (DVB), and 3.02 g benzoyl peroxide (BPO) was prepared in an 800 mL beaker. This solution was sparged with nitrogen for 5 minutes by stirring the solution with a pasteur pipette connected to a nitrogen tank. The aqueous phase was prepared in an 800 mL beaker with 17.93 g PADMAC, 9.507 g boric acid, and 316.5 g distilled water. In a 400 mL beaker, 1.45 g of Pharmagel was dissolved in 158.27 g distilled water and warmed to 50° C while continuously stirring. The two aqueous solutions were then mixed together, and the pH of the resulting solution was adjusted to 10.3 with 50 % NaOH. The apparatus used for the polymerization consisted of a condenser, nitrogen inlet with bubbler, and thermometer attached to a 1000 mL round

bottom flask. An overhead stir apparatus with its shaft and blade inside of the round bottom flask completed the assembly.

The aqueous phase was poured into the round bottom flask, the stir speed was set at 307 rpm, and the blade was adjusted to be slightly above the aqueous phase. The round bottom was sparged with nitrogen for about 10 min. The organic phase was then added to the round bottom flask, and the nitrogen sweep was continued. The stir motor was turned on for 2 min, and during the 1 min rest period, the solution was checked for the formation of beads. This was done by the use of a light to determine that the beads were spheres of organic phase in aqueous solution and not vice versa. This cycle was repeated two more times. The round bottom flask was heated to 80° C over a 2 hour period by increasing the temperature 7° C every 15 minutes. The temperature was controlled by a thermowatch sensor clipped to the thermometer, and the round bottom was heated by a lamp. The polymerization continued for 10 hrs at which time the heat lamp and stir motor were turned off.

The mixture in the round bottom was then refluxed for two hours after the addition of 100 mL distilled water. The nitrogen sweep was turned off, and the nitrogen inlet and condenser were removed. The solution was removed with a pasteur pipette connected to an aspirator. The beads were washed once with 1×10^{-4} N HCl solution and three times with distilled water. Each wash cycle consisted of a 15 minute stir time; the solution was removed with a magic wand before the next wash cycle. The beads were then Buchner dried for 5 min and extracted with a Soxhlet apparatus in toluene for 17 hrs. The resin was then air dried and sieved to isolate the -40 + 60 sized beads.

The procedures for the polymerization of polystyrene were almost identical to those followed for the preparation of the poly(vinyl benzyl chloride) resins. The masses of the reagents used for the polystyrene synthesis were as follows: 286.28 g styrene, 10.84 g DVB, and 3.0 g BPO for the organic phase; 17.86 g PADMAC, 0.9494 g boric acid, and 316.5 g distilled water for the first aqueous solution; and 1.44 g Pharmagel and 158.27 g distilled water for the second aqueous solution. The pH of the combined aqueous solution was adjusted to 10.0 with 50 % NaOH. The stir motor was set at 365 rpm. White chaff was produced during the polymerization so the solution was washed four extra times with distilled water. The resins were dried for 18 hrs in a 110° C oven

then sifted to isolate the -40 +60 size beads. These were then extracted with toluene in a soxhlet apparatus for 17 hrs and allowed to air dry.

Arbusov Reaction/ Hydrolysis

The phosphonic acid resins were prepared by the Arbusov reaction followed by hydrolysis of the poly(vinyl benzyl chloride) resins. This reaction was performed in a 500 mL three-neck round bottom flask. First 150 mL of triisopropyl phosphite was added to 9.99 g of poly(vinyl benzyl chloride) resins. This mixture was stirred with an overhead stir apparatus set at 227 rpm and refluxed for 17 hrs by heating with a heat lamp. The solution was removed from the beads with a magic wand, and the beads were washed with acetone twice and with dilute HCl twice. Each wash cycle consisted of a 15 minute stir time; the solution was removed with a magic wand before the next wash cycle.

The hydrolysis of the resins was accomplished by the addition of 150 mL of concentrated HCl to the round bottom flask. The mixture was refluxed for 24 hrs by heating with a lamp. After the hydrolysis, the resins were conditioned in a glass frit with 1 L successively of water, 4 wt % NaOH, water, 4 wt% HCl, and water. This phosphonic acid resins (RK-01-015) were stored under water. Before use in the metal ion studies, these beads were reconditioned.

Chlorosulfonation

The sulfonated phosphonic acid resins were prepared by the chlorosulfonation of the phosphonic acid resins. Azeotrope distillation of 11.09 g of the phosphonic acid resins in heptane was performed for three hours. The water was removed by the use of a Dean-Stark trap. The heptane was removed by Buchner drying the resins which were then returned to the round bottom flask. The beads were immersed in 200 mL of ethylene dichloride (EDC) for an hour before the reaction to effectively swell them. The round bottom flask was placed on ice for about 5 minutes, and then a mixture of 146.4 mL EDC and 36.6 mL chlorosulfonic acid was added to the round bottom via an addition funnel. The mixture was allowed to drip slowly into the reaction vessel. After the addition of the acid mixture was completed, the ice and funnel were removed. The

mixture was stirred at room temperature for 48 hrs. A magic wand was used to remove the solution, and the beads were subjected to the following washing cycle: pure dioxane, 10 % water/ 90 % dioxane, 25 % water/ 75 % dioxane, 50 % water/ 50 % dioxane, and finally pure distilled water. Each cycle consisted of a 20 minute stirring time with 100 mL of each solution; the solution was removed before the start of each new wash cycle. The sulfonated phosphonic acid resins (RK-01-017) were conditioned (see above), extracted with water in a soxhlet apparatus for 18 hrs, reconditioned, and stored under water.

Friedel-Crafts Reaction

The Friedel-Crafts reaction of the polystyrene resins with bromoacetyl bromide was the first reaction of a series to produce the β -ketophosphonic acid resins. In a 500 mL three-neck round bottom flask, 9.86 g of polystyrene resin was contacted with 40.0 mL of carbon disulfide (CS_2) and allowed to swell overnight. The round bottom flask was immersed in ice, and the following reagents were added in this order: 40 mL CS_2 , 39.93 g AlCl_3 , 25.5431 g bromoacetyl bromide, and finally 20 mL CS_2 . The mixture turned orange with the addition of the AlCl_3 and then red with the addition of the bromoacetyl bromide. The mixture was stirred for 48 hrs; the round bottom flask was kept on ice for the first 3 hrs of the reaction. The solution was removed with a magic wand, and the following wash cycle was applied (similar to above) with 200 mL of each solvent: ice ethanol (1/4 part ice), water, 10 % acetic acid, and ethanol. The resins were dried while still in the flask in a vacuum oven at 70° C.

The Perkow reaction was then performed on the beads (analogous to an Arbusov reaction) with 100 mL of triisopropyl phosphite. After this reaction, the beads were washed three times with dilute HCl solution then were subjected to hydrolysis with concentrated HCl (as above). The resulting β -ketophosphonic acid resins (RK-01-039) were washed in water, conditioned, extracted with water in a soxhlet apparatus for 17 hrs, reconditioned, and stored under water.

The sulfonated β -ketophosphonic acid resins (RK-01-048) were produced by the azeotrope distillation of 10.07 g of the β -ketophosphonic acid resins followed by chlorosulfonation (as above). The acidic solution consisted of 132.9 mL EDC and

33.23 mL chlorosulfuric acid. The resins were washed in water, conditioned, extracted with water in a soxhlet apparatus for 17 hrs, reconditioned, and stored under water. The resins had broken up into fractured particles by the time of the second conditioning.

Determination of % solid

A 20 mL scintillation vial was dried in a 110° C oven for several hours and then cooled in a dessicator. A 1~1.5 g sample of Buchner dried beads was weighed accurately into the vial and was dried for 17 hrs in the 110° C oven. The mass of the resin was determined before and after drying, and the % solid of the resin was calculated as follows:

$$\% \text{ solid} = (\text{mass dry sample} / \text{mass wet sample}) \times 100$$

Determination of Acid Capacity

About 1~1.5 g of Buchner dried resin was weighed into a 200 mL ground glass Erlenmeyer flask. A stir bar was added, and 200 mL of 0.1289 N NaOH solution was pipetted into the flask. The contents of the flask were allowed to stir at 350 rpm on a multi-point stirrer for 17 hrs. Two 50 mL aliquots of the resulting basic solution were titrated with a 0.1602 N HCl solution. The acid capacity was calculated as follows:

$$\text{Acid capacity (meq/g)} = ((\text{vol NaOH})(\text{N NaOH}) - 4(\text{vol HCl})(\text{N HCl}))/ \text{mass dry resin}$$

Determination of Phosphorus Capacity

Two samples of each resin were prepared. First, 20-25 mg oven dried resin was carefully weighed into a clean, dry 125 mL Erlenmeyer flask. Then 400 µl 0.5 M copper sulfate and 10 mL of concentrated sulfuric acid were added to the flask. The solution was heated until clear. After the solution had cooled to room temperature, about 75 mL of distilled water and 2.0 g of potassium persulfate were added. The solution was then heated at just below boiling temperature for about 2 hrs. The solution was cooled to room temperature, and its pH was adjusted to ~7 by the addition of 50 % NaOH first and then 2 % sulfuric acid. The solution was carefully transferred to a 100 mL volumetric flask; the original flask was rinsed with distilled water which was also transferred to the

volumetric flask. The solution was brought up to volume with distilled water and mixed well. After mixing, 25 mL of the solution was transferred to a 50 mL volumetric flask, 10 mL of a Vanadate-Molybdate solution was pipetted into the flask with an automatic pipette, and the solution was diluted to mark with distilled water. A blank was also prepared by the dilution of 10 mL of the Vanadate-Molybdate solution in a 50 mL volumetric flask. A Spec-21 was zeroed with the blank solution, and the absorbance of the sample were determined. The phosphorus capacity was calculated as follows:

$$\text{mg P} = (\text{absorbance} - \text{intercept}) / \text{slope}$$

(The intercept and slope were determined from the calibration of the instrument.)

$$\text{P capacity (meq / g)} = (\text{mg P} \times 4) / (30.974 \times \text{mass dry resin})$$

Metal Ion Studies

Buchner dried resin was carefully weighed into a 20 mL scintillation vial. The mass of resin needed was calculated by:

$$\text{Mass required} = (1 / \text{P capacity}) / \% \text{ solid}$$

The resin was solvent exchanged for 15 min four times with 1 N HNO₃ solution. After each period, the solvent was removed by a pasteur pipette attached to an aspirator via a side arm flask. The resin was contacted with 10 mL of 1 x 10⁻⁴ N metal solution in 1 N HNO₃ after the four periods with the blank solution. After the contact time (½ hr or 24 hrs), the metal solution was transferred to a clean 20 mL scintillation vial with a pasteur pipette. The solutions were then analyzed with atomic absorption spectroscopy (for copper and lead) and atomic emission spectroscopy (for europium). The absorbance (or emission) given by the Perkin-Elmer spectrophotometer for each solution was compared to the results from standard solutions of each metal. Four standard solutions were used for each metal with these concentrations: 1 x 10⁻⁴, 5 x 10⁻⁵, 2 x 10⁻⁵, and 1 x 10⁻⁵ N metal in 1 N HNO₃. The europium solutions were spiked with a KCl solution to suppress ionization of the europium.

Results and Discussion

The % solid, acid capacity, and phosphorus capacity of each resin is given. The theoretical phosphorus capacity is also shown. The acid capacity should be about twice the phosphorus capacity for the non-sulfonated resins (RK-01-015, RK-01-039) and about three times that of the phosphorus capacity for the sulfonated resins (RK-01-017, RK-01-048). The acid and phosphorus capacity values indicate the degree of functionalization of the benzene rings of the polymer. A correlation between the theoretical and experimental phosphorus capacities indicates that most of the rings has been phosphorylated.

Resin	% solid	Acid Capacity (meq/ g)	Phosphorus Capacity (meq/ g)	Theoretical Phosphorus Capacity (meq/ g)
RK-01-015	51.61	9.728	4.696	4.864
RK-01-017	32.65	10.089	3.455	3.501
RK-01-039	32.31	2.799	1.614	4.325
RK-01-048	17.22	3.643	0.955	3.213

The resins RK-01-039 and RK-01-048 were not fully functionalized as shown by the difference in the theoretical and experimental phosphorus capacities. The acid capacity of the RK-01-048, which is greater than three times the phosphorus capacity, indicates that some of the originally non-phosphorylated benzene rings in the resin were sulfonated during the following chlorosulfonation reaction.

The decrease in the % solid values between RK-01-015 and RK-01-017 and between RK-01-039 and RK-01-048 indicate that more solvent (water) is being attracted inside the sulfonated resins. This is due to the ability of the sulfonic acid ligand to increase the hydrophilicity of the resin.

Metal Ion Studies

The results of the metal ion studies of each resin with europium(III), copper(II), and lead(II) are given for the ½ hr and 24 hr contact times. The equations used for determining the % M absorbed, r, c, and D are provided in the appendix.

Europium (III): ½ hr contact time

Resin	Wet Mass (g)	% Solid	Dry Mass (g)	% M Absorbed	r	c	D
RK-01-015	0.4085	51.61	0.2108	6.23	0.0003	0.00009	3.15
RK-01-017	0.9217	32.65	0.3009	91.45	0.0030	0.00001	355.21
RK-01-039	1.7379	32.31	0.5615	45.42	0.0008	0.00005	14.82
RK-01-048	0.5044	17.22	0.0869	95.51	0.0110	0.00000	2451.70

24 hr contact time

Resin	Wet Mass (g)	% Solid	Dry Mass (g)	% M Absorbed	r	c	D
RK-01-015	0.4083	51.61	0.2107	19.00	0.0009	0.00008	11.13
RK-01-017	0.9212	32.65	0.3008	94.61	0.0031	0.00001	583.10
RK-01-039	1.7371	32.31	0.5613	64.30	0.0011	0.00004	32.09
RK-01-048	0.5038	17.22	0.0868	96.34	0.0111	0.00000	3038.41

Copper (II): ½ hr contact time

Resin	Wet Mass (g)	% Solid	Dry Mass (g)	% M Absorbed	r	c	D
RK-01-015	0.4084	51.61	0.2108	5.80	0.0003	0.00009	2.92
RK-01-017	0.9210	32.65	0.3007	23.11	0.0008	0.00008	10.00
RK-01-039	1.7376	32.31	0.5614	14.79	0.0003	0.00009	3.09
RK-01-048	0.5091	17.22	0.0877	12.62	0.0014	0.00009	16.48

24 hr contact time

Resin	Wet Mass (g)	% Solid	Dry Mass (g)	% M Absorbed	r	c	D
RK-01-015	0.4086	51.61	0.2109	3.70	0.0002	0.00010	1.82
RK-01-017	0.9213	32.65	0.3008	25.88	0.0009	0.00007	11.61
RK-01-039	1.7378	32.31	0.5615	16.18	0.0003	0.00008	3.44
RK-01-048	0.5007	17.22	0.0862	12.62	0.0015	0.00009	16.75

Lead (II): ½ hr contact time

Resin	Wet Mass (g)	% Solid	Dry Mass (g)	% M Absorbed	r	c	D
RK-01-015	0.4089	51.61	0.2110	2.35	0.0001	0.00010	1.14
RK-01-017	0.9218	32.65	0.3010	24.54	0.0008	0.00008	10.80
RK-01-039	1.7373	32.31	0.5613	16.68	0.0003	0.00008	3.57
RK-01-048	0.5068	17.22	0.0873	47.33	0.0054	0.00005	102.95

24 hr contact time

Resin	Wet Mass (g)	% Solid	Dry Mass (g)	% M Absorbed	r	c	D
RK-01-015	0.4084	51.61	0.2108	8.82	0.0004	0.00009	4.59
RK-01-017	0.9213	32.65	0.3008	28.47	0.0009	0.00007	13.23
RK-01-039	1.7379	32.31	0.5615	16.68	0.0003	0.00008	3.56
RK-01-048	0.5089	17.22	0.0876	52.05	0.0059	0.00005	123.86

The results of the metal ion studies show that the sulfonated resins are more effective in extracting metal ions from solution than the others for all metals. Likewise, the β -ketophosphonic acid resins tend to show a greater capacity for the metals than the phosphonic acid resins. Both the phosphonic acid and β -ketophosphonic acid resins achieve the greatest complexation with the europium(III) ions.

The sulfonated forms of the resins (RK-01-017, RK-01-048) are more effective in extracting the metals from solution because they create hydrophilic areas within the hydrophobic resin which allows the metals increased access to the phosphonic acid coordinating sites. The β -ketophosphonic acid resins have a greater ability to attract the metals because the carbonyl oxygen near the phosphoryl oxygen helps to coordinate the metal.

The extraction of the europium(III) metal ions is the greatest of the three metals because the soft acid nature of the ions complements the soft base nature of the phosphoryl oxygen. Lead(II) ions are not as soft as the europium(III) ions, but they are complexed to a greater extent than the copper(II) ions which are hard acids.

Mixtures of metals were not analyzed in this project. However, from the results of previous studies, an assumption is made that the metals do not influence each other's ability to complex with the phosphonic acid sites in the resin.

Conclusions

The β -ketophosphonic acid resins were shown to have a higher capacity for the metal ions studied in this project than the phosphonic acid resins. This indicates that the sulfonated β -ketophosphonic acid resin would offer an improvement over other resins currently in use. However, the fractionation of the RK-01-048 resin during synthesis must be studied; if these resins are to be used commercially, they must be able to withstand the high pressures and regeneration methods that are used in industrial processes. It may also be beneficial to study mixtures of metal ions such as those which are normally encountered in industry to insure that the results for the individual metal ion studies can be reproduced. This project is one of many, many steps in the study of the possible applications of ion exchange resins. The synthesis and characterization of these new resins will supplement existing knowledge of the subject.

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Appendix

Equations used in the metal ion studies

$$\% \text{ M absorbed} = (\text{initial conc.} - \text{final conc.}) / \text{initial conc.} \times 100$$

$$\text{Meq absorbed} = (\% \text{ M absorbed} / 100) \times \text{initial conc.} \times 10 \text{ mL}$$

$$r = \text{Meq absorbed} / \text{dry mass}$$

$$\text{Meq free} = \text{initial conc.} \times 10 \text{ mL} - \text{Meq absorbed}$$

$$c = \text{Meq free} / 10 \text{ mL}$$

$$D = r / c$$

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Synthesis and Characterization of Sulfonated β -Ketophosphonate Ion Exchange Resins

Ryoko Kita

Ion exchange resins were first used in the 1930's. Since then, they have increased in durability and versatility. Many ion exchange resins are now used commercially for the separation, purification, and concentration of targeted species in such fields as food processing, water remediation, and catalysis.

Sulfonated β -ketophosphonate ion exchange resins were prepared and characterized. These resins were compared to the β -ketophosphonic acid, phosphonic acid, and sulfonated phosphonic acid ion exchange resins as controls. The ability of these resins to complex europium(III), copper (II), and lead(II) was tested with metal ion studies with durations of $\frac{1}{2}$ hr and 24 hrs for each metal. When the resins were compared, the sulfonated resins exhibited a higher tendency to complex the metal ions than the non-sulfonated resins. This tendency was the most significant in the complexation of europium(III); the sulfonated β -ketophosphonic acid resin was the most efficient of the resins in extracting this metal.