Metal specific hydroxyoxime ion-exchange resins

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The preparation of specific ion-exchange resins containing hydroxyoxime groups is described. These were prepared from substituted phenyl acrylate polymers via the Fries rearrangement. Analysis suggests that the beads contain carboxylic acid groups as well as hydroxyoximes. Uptake of copper at different pH values suggests that the hydroxyoximes form 1:1 complexes with copper ions.

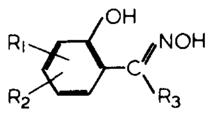
Keywords Ion-exchange; poly(phenyl acrylate); hydroxyoxime; Fries rearrangement; copper extraction; poly(phenyl vinyl ketone)

INTRODUCTION

The recovery and concentration of metal ions from aqueous solution has been the subject of much effort by both industry and government. The solvent extraction of metals such as copper from solutions derived from the leaching of ores is well established commercially[1]. However, because of the large volumes of liquids involved, solvent extraction has not generally been applied successfully to very dilute solutions such as are derived from mine waste streams and as occur in liquid effluents from various industrial processes. The solvent extraction process also needs large volumes of inflammable solvent and a very large plant area. One alternative technique of metal recovery which may have advantages under some circumstances is selective ion-exchange using crosslinked polymer resins.

Chelating ion-exchange resins have been the subject of a number of reviews[2,3]. Much of the previous work has been on the modification of polystyrene beads including macroporous systems. Various condensation polymers have also been tried. Resins impregnated with ligands have also been used[4] though in such systems loss of ligand during extraction could occur and the overall copper uptake per gram of resin is limited by the presence of inert material.

Hydroxyoximes with a general formula:



where R_1, R_2 and R_3 can be a wide range of substituent groups, are known to form complexes with metals such as copper in a 2:1 ratio[5].

In this paper we describe the preparation of ion-exchange resins containing hydroxyoxime groups similar to the above. The equilibrium metal uptake has been measured under various conditions and this has been interpreted in terms of the considered composition of the resin.

EXPERIMENTAL

The proposed reaction scheme is shown in *Figure 1*. Substituted phenyl acrylates with a general formula (I) are prepared. Of the substituents, A and B, A may be hydrogen but B may not. The monomers are suspension polymerized in the presence of a crosslinking agent to form beads, the main chain units of which are (II). The beads are then reacted in a Fries rearrangement and the

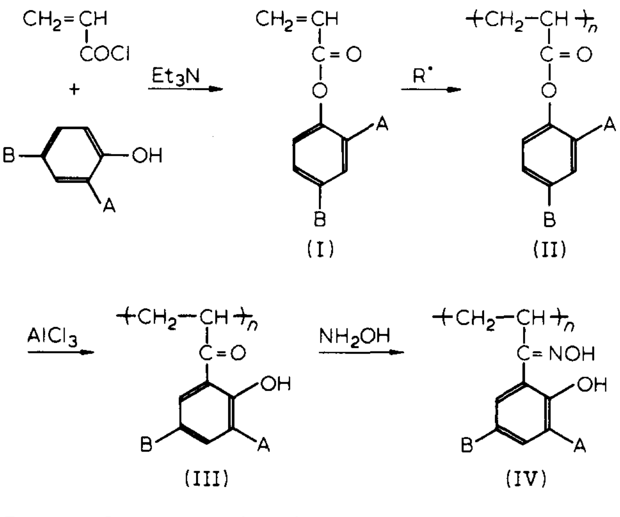


Figure 1 Proposed reaction scheme

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resulting aryl ketones (III) oximated to give the desired product (IV).

The Fries rearrangement often leads preferentially to substitution *para* to the ester group, but because this position is blocked, *ortho* substitution occurs.

Preparation of 4-methyl-2-nitrophenyl acrylate

4-Methyl-2-nitrophenol (0.2 moles, A.R.), triethylamine (0.2 moles, A.R.), and benzene (100 cm^3, A.R.) were placed in a 500 ml flask equipped with a stirrer and maintained in an ice bath. Acryloyl chloride (0.22 moles, A.R., *CAUTION*-possible potent carcinogen) was added dropwise over one hour. The temperature was allowed to reach ambient and the flask left overnight. The solution was then filtered and the precipitate washed with benzene. The filtrate was washed with saturated sodium bicarbonate solution and then twice with distilled water. The solution was dried over calcium chloride, decanted, and the solvent removed by distillation under reduced pressure to leave a brown crystalline mass (35.5 g). The product was recrystallized from methanol to give 28 g of pale yellow crystals (68% yield) m.p. 48°C. Analysis gives C, 57.81; H, 4.41; N, 6.78 against theoretical values C, 57.97; H, 4.34; N, 6.76.

Alternative preparation

The commonest and most convenient method of preparation of higher acrylates is by ester exchange using the methyl ester[6]. Unfortunately this did not appear to work for the phenyl acrylates. Because of the acidity of the phenol the preparation is more like that of an acid anhydride. However it is possible to do an 'acid exchange' under similar conditions.

4-Methyl-2-nitrophenol (10.88 g), acetic anhydride (8.1 g, A.R.) and tetrachloroethylene (75 cm^3, A.R.) were placed in a flask and the mixture refluxed for 30 minutes. Acrylic acid (7.00 g, A.R.) was then added and the mixture distilled through a packed column at a pressure of 150 mm Hg. An acetic acid/tetrachloroethylene azeotrope distilled off at 57°–59°C. The head temperature was then allowed to rise to 64°C to remove the solvent. The product was then dissolved in 1,1,1-trichloroethane and washed with saturated sodium bicarbonate solution. It was then washed with distilled water and the solution dried over calcium chloride. The solvent was removed under reduced pressure and the product recrystallized from methanol to give 11.9 g of yellow crystals m.p. 48°C (yield 72%).

Preparation of 4-chlorophenyl acrylate

For some purposes, especially ease of analysis, the hydroxyoximes prepared from this ester were preferable to those from the nitro compound. It was prepared using the same method as for the nitro compound using the same molar equivalents, but using 4-chloro phenol to give an oily product, m.p. 6°C. Analysis gave C, 60.57; H, 4.17. Theory requires C, 59.18; H, 3.84.

Preparation of polymer beads

A 500 cm^3 baffled flanged flask was equipped with an efficient paddle stirrer, a nitrogen bleed, and a condenser. Into it was placed distilled water (300 cm^3) in which had been dissolved sodium sulphate (5 g as anhydrous A.R. salt) and poly(vinylpyrrolidone) (0.65 g, commercial). 4-Methyl-2-nitrophenyl acrylate (48.7 g), divinylbenzene (4 cm^3, or as required, used as a 50:50 mixture with ethylvinylbenzene) and azobisisobutyronitrile (0.1 g) were added and the mixture stirred in a water bath at 75°C for 48 h. The resulting beads were filtered off and washed with first water, then methanol, and then dried. The yield was 42.1 g, 86% based on monomer.

Analogous preparations were carried out using the 4-chlorophenyl acrylate. The reaction appeared to be quicker (NO$_2$ compounds are polymerization retarders) and generally gave better yields of at least 95%. In each case the beads were less than 0.5 mm in diameter.

Fries rearrangement of polymer beads

Poly(4-methyl-2-nitrophenyl acrylate), (10.8 g of crosslinked beads) was mixed with nitrobenzene (15 cm^3, A.R.) in a flask which was cooled in an ice bath. To the flask was slowly added aluminium chloride (3.1 g, anhydrous, crushed) forming a bright red complex. The slurry so formed was added to a 250 cm^3 flask containing methyl cyclohexane (100 cm^3, A.R.) maintained at 100°C in a steam bath. The mixture was allowed to react for 96 h. The resulting beads were filtered off and washed several times alternately with water, 10% of concentrated hydrochloric acid, and methanol. 5.47 g of beads were recovered.

The yield and composition of the resultant beads was highly dependant on the time, temperature, mole ratio of aluminium chloride, and mode of addition of the various components as will be discussed later.

An analogous reaction was performed using the poly(4-chlorophenyl acrylate) beads. An improved product with better copper uptake was formed if 50 mole per cent AlCl$_3$ was used instead of 40 mole per cent in the previous example.

Oximation of product of Fries rearrangement

The beads, from the rearrangement of the poly(4-methyl-2-nitrophenyl acrylate) beads (5 g), were placed in a 100 cm^3 round bottom flask. To them was added absolute ethanol (50 cm^3, A.R.), pyridine (5 cm^3, A.R.) and hydroxylamine hydrochloride (5 g, A.R.). The flask was kept in a water bath at 70°C overnight. The beads were filtered off and washed with water and methanol to yield 4.75 g of product.

The other beads were treated in an analogous manner.

Formation and decomposition of copper complexes

The beads were placed in a column through which was slowly passed a solution of copper sulphate at 6.0 g dm^{-3} adjusted to the required pH. This was continued until the eluate was at the same pH as the feed (copper displaces hydrogen from a hydroxyoxime). Further contact with the solution overnight produced no increase in absorption.

The copper complex was decomposed by stripping with sulphuric acid (150 g dm^{-3}) and hence the adsorbed copper recovered. The copper concentration was determined by titration of the neutralized aqueous samples against sodium thiosulphate (using iodine liberated from potassium iodide and a starch indicator).

The above process was used to measure the maximum copper uptake. In order to study the adsorption process, however, we needed to find the fraction of copper adsorbed from solution at a given pH under conditions where the free ligand concentration remained virtually constant, i.e. at very low copper to ligand ratios. In these experiments the beads were contacted with dilute copper solutions (10^{-3} mol l^{-1}) and at such relative quantities that never more than ten per cent of the ligand groups could be complexed. The residual copper in the solutions was determined by atomic absorption spectroscopy.

Analysis of products

Because the beads in effect contain all the by-products of the Fries rearrangement as well as the required ligand group and units of the crosslinking agent, and cannot be purified, the analysis involved formidable problems. This is compounded by the fact that the beads are insoluble solids which makes many analytical techniques impossible to use.

Elemental analysis is only of limited use for such indeterminate mixtures. The chlorine containing beads in principle would be better because of the extra information a chlorine analysis could give. However, results of elemental analysis were often irreproducible, we think due to incomplete burning of the beads and this appeared to be worse for the chlorine containing compounds.

We expect that the other main group in the beads would be acrylic acid units from the hydrolysis of the ester and on this basis we can titrate the beads against alkali and obtain an estimate of the number of such groups.

Another technique which can be used for analysis of these products is carbon-13 n.m.r. This has the advantage over proton n.m.r. that there is larger separation of peaks and reasonable spectra can be obtained even in crosslinked systems (our polymers crosslink during the Fries rearrangement even in the absence of divinyl benzene).

The problem in obtaining quantitative carbon-13 spectra is that different carbon atoms can have very different spin-lattice relaxation times and under the normal rapid pulsing conditions those giving longer relaxation times would have a lower than expected intensity. Another problem is the peak enhancement due to the 'Nuclear Overhauser Effect' caused by the use of broadband proton decoupling. The problems were overcome in this case by using a long repetition time and introducing a delay between pulses and only switching on the decoupler whilst data are being acquired. Spectra were taken on a 'Bruker Spectrospin, 22.67 MHz machine using a 40 s repetition time, having the decoupler on from 0 to 0.8 s and collecting data from 0 to 0.68 s. The samples were of a lightly crosslinked resin from the chlorine containing ester with only 1% crosslinking agent. These were swollen in D_2O and sodium hydroxide and a dioxan standard was introduced.

The last piece of data from which analytical inferences can be made is the copper uptake itself and its variation with pH. This will be discussed later.

The carbon-13 spectra, of a 1% crosslinked chlorine compound is shown in *Figure 2*. It shows a peak at 185.6 (ppm c.f. TMS) attributed to CO_2H and at 169.4 attributed to $C=NOH$. It also showed peaks at 166.1, 130.1, 120.9 and 118.6 ppm attributed to aromatic carbons, and broad bands between 55 and 25 attributed to the backbone carbons. Because of the long repetition time we achieved only a poor signal to noise ratio and the integral was not very accurate. However, one could conclude that the product mostly consisted of acrylic acid units and the required oxime units and that the former outnumber the latter by between 2:1 and 3:1 on a molar basis.

Our most reliable elemental analysis of this resin, by oxidizing under the most extreme conditions possible, is shown below and is compared with theoretical values for 2:1 and 3:1 (acid:desired product) resins. We also show experimental values for a resin derived from 4-methyl-2-

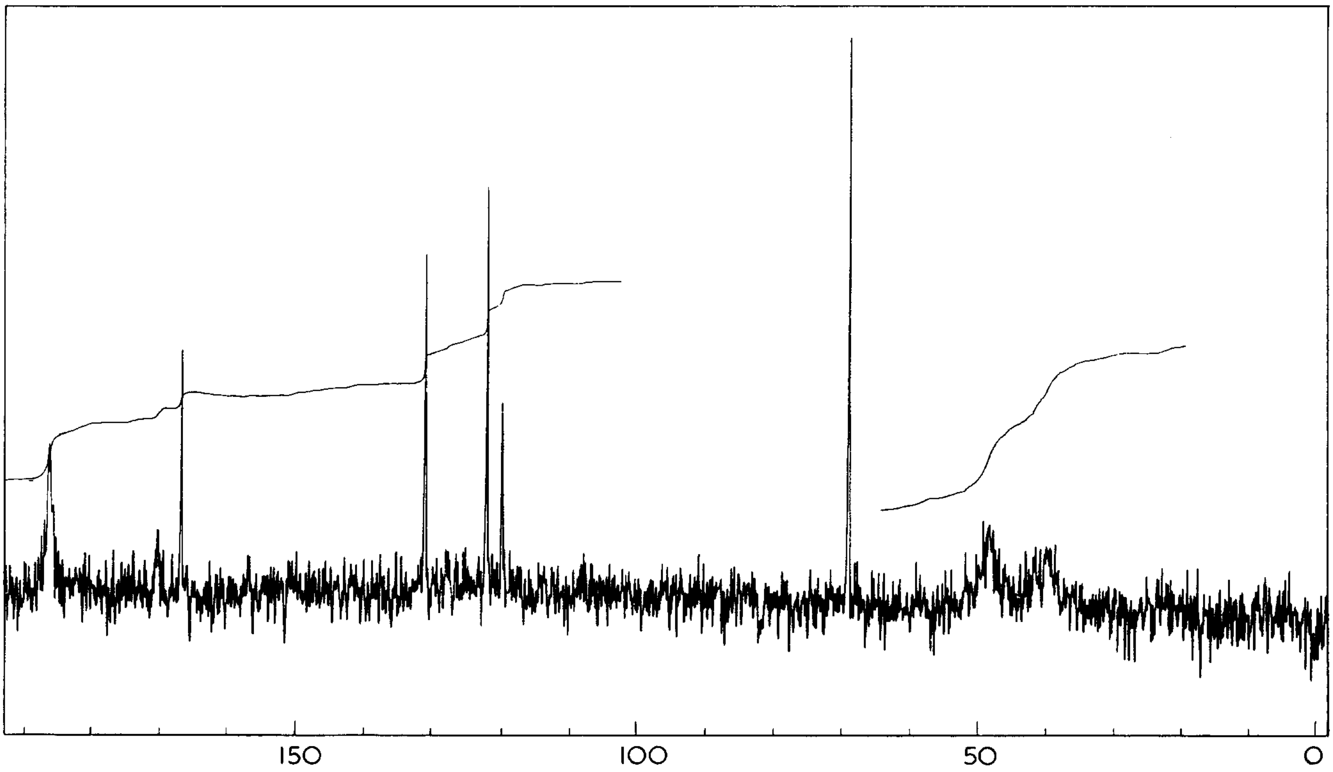

Figure 2 Carbon-13 spectra of a resin derived from 4-chlorophenyl acrylate with 1% crosslinking agent. The peak at 67.4 is from dioxan by which the spectra was set

Table 1 Elemental analysis

	(Chloro)	Theory		(Nitro)	Theory
	Experimental	2 : 1 acid	3 : 1 acid	Experimental	3 : 1 acid
Carbon	48.4	52.7	52.2	53.7	52.05
Hydrogen	4.4	4.7	4.8	5.7	5.02
Nitrogen	2.3	4.1	3.4	4.0	6.39
Chlorine	10.4	10.4	8.6		

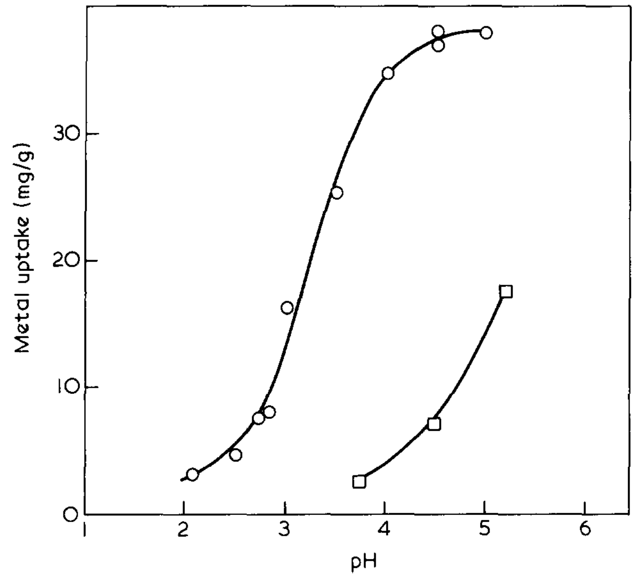

Figure 3 Metal uptake against pH for beads derived from 4-methyl-2-nitrophenyl acrylate, ○ = copper uptake, □ = iron (ferrous) uptake

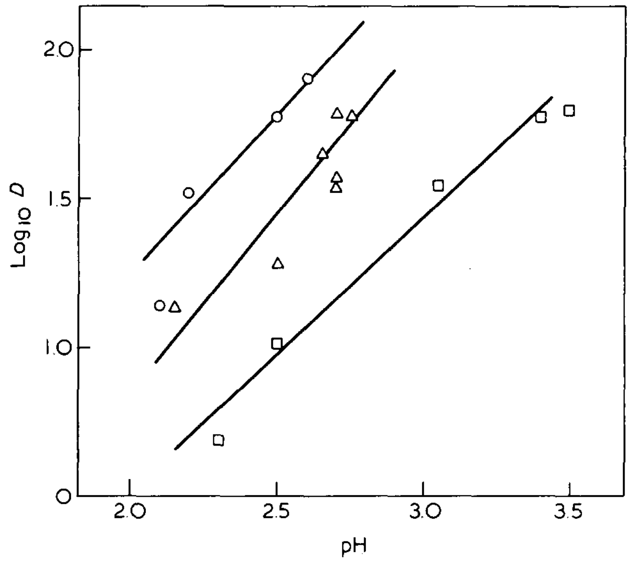

Figure 4 Plots of log *D* against pH for resins derived from △ = 4-methyl-2-nitrophenyl acrylate, ○ = 4-chlorophenyl acrylate with 4% crosslinking agent, □ = 4-chlorophenyl acrylate with 1% crosslinking agent.

nitrophenyl acrylate together with a theoretical value for a 3:1 acid:oxime mixture.

Considering the other byproducts which may be present this is quite good though the experimental nitrogen value is rather low. It was also observed that the peak in the C-13 spectra attributed to the oxime was relatively low (~60–80%) compared to the aromatic carbons. This suggests that for some reason some carbonyl groups which have not been converted to an oxime remain in the resin.

Titration of acid groups shows the product to consist of 38% by weight acrylic acid units equivalent to a ratio of 1.68:1 on a molar basis, in reasonable agreement with the above results.

We would conclude that the resin probably consists predominantly of acrylic acid units and aromatic units in an approximate 2:1 ratio with over half of the aromatic units containing oxime groups. These are expected to be the desired hydroxyoxime groups though other byproducts containing oxime groups are also possible.

RESULTS AND DISCUSSION

Figure 3 shows the results for the maximum copper uptake of resins prepared from 4-methyl-2-nitrophenyl acrylate, from copper sulphate at 6.0 g dm^{-3}, and the comparable result for iron (ferrous sulphate) which does not form strong complexes with hydroxyoximes. The maximum copper uptake under these conditions was 38 mg/g resin. The corresponding figure for the chlorine containing analogue was 36 mg/g resin for a resin containing 4% divinyl benzene crosslinking agent and 44 mg/g resin for one with only 1% crosslinking agent.

From what is known of such complexes one would expect the hydroxyoxime to hold copper at much lower pH values. The curve for uptake should also be much steeper and this tells us much about the nature of the complex.

For an equilibrium, if we can assume that all ligand groups are equivalent:

$$n\,\mathrm{LH} + \mathrm{Cu}^{++} \rightleftarrows \mathrm{L}_n\mathrm{Cu}^{(2-n)+} + n\mathrm{H}^+$$

$$K\ \mathrm{eqn} = \frac{[\mathrm{L}_n\mathrm{Cu}^{(2-n)+}][\mathrm{H}^+]^n}{[\mathrm{LH}]^n[\mathrm{Cu}^{++}]}$$

If we define *D* as:

$$D = \frac{\mathrm{Cu\,(complexed)}}{\mathrm{Cu\,(in\ solution)}}$$

then

$$\log D = \log K + n \log[\mathrm{LH}] + n\,\mathrm{pH}$$

In the experiments carried out with dilute copper concentrations, and only light loadings of the ligand, [LH] can be considered constant and a plot of log *D* against pH should give a straight line of slope *n*.

Figure 4 shows plots of log *D* against pH for the 4-methyl-2-nitrophenyl derivative and the 4-chlorophenyl derivative, the latter with 1% and 4% crosslinking agent.

The gradients and correlation coefficients were 1.09 (corr 0.90), 1.00 (corr 0.87) and 0.96 (corr 0.99) respectively which suggests the formation of a 1:1 complex. This contrasts with the 2:1 complexes formed by low molecular weight hydroxyoximes[5].

The difference might be explained by the overall entropic and steric restrictions in the resin, by the environment of the hydroxyoxime in the resin (water, polymer, carboxylic acid groups), or by specific local steric restrictions in this particular hydroxyoxime group. In particular the high concentration of carboxylic acid groups may contribute to the adsorption or replace one hydroxyoxime group in the coordination complex.

Another possible explanation would be the existence of several different types of ligand groups or environments. This might spread out the adsorption process over a range of pH and give the impression of a 1:1 complex forming process. We believe, however, that it would be unlikely that all the results would come so close to 1:1.

CONCLUSIONS

We have successfully synthesized a copper specific ion-exchange resin. We have inferred from the analysis that the major constituent groups in the resin are carboxylic acids and hydroxyoximes. The copper uptake at different pH values suggests that the hydroxyoximes form 1:1 complexes with copper ions unlike low molecular weight hydroxyoxime ligands.

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