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Metal–Metal Chelating Ion-Exchange Processes on 8-Hydroxyquinoline and 8-Hydroxyquinaldine Resins

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Abstract

The metal capacity vs pH contours and the separation ratios for copper, zinc, and aluminum have been studied for an oxine-containing, chelating ion-exchange resin. Metal–metal exchange studies on this resin involving the three metals have demonstrated that this is not a simple substitution process, sorption and desorption of the ions being controlled by solution concentration. The sterically hindered ligand, 8-hydroxyquinaldine, incorporated in a resin, demonstrated much greater selectivity for other metals over aluminum and confirmed published solvent extraction data for this ligand.

With the development of methods whereby chelating ion-exchange resins having the desirable properties of high total capacities and fast kinetics may be prepared reproducibly (*1*) by polycondensation reactions with formaldehyde, progress may now be made in the application of such materials to separation problems. The preparation of an 8-hydroxyquinoline (oxine) resin has been studied extensively (*2*, *3*), and conditions given for the production of a resin with optimum performance. The oxine chelating resin has been described many times in the literature since the first synthesis was described by Von Lillin (*4*), and several investigations of its metal separating possibilities have been carried out. The separation of uranyl ions from chromium, cobalt, and aluminum has been suggested (5), and separations of iron, copper, and uranyl ions from cobalt, nickel, aluminum, and zinc have been carried out (*6*). Many separations however, are either not possible or have so far not been explored. These include copper from iron, nickel from cobalt, and aluminum from zinc. These separations in fact belong to the class of separations which have, so far, not proved possible. Examination of total capacity vs pH contours for the exchanger with a metal ion species gives a certain amount of information, on the magnitude of the metal–resin complex stability, for example. Thus, from the widely differing pH values at which appreciable metal capacities are demonstrated, separations such as iron from cobalt and nickel or aluminum from magnesium are indicated (*6*). An interesting study would be a comparison of oxine- and 2-methyl-8-hydroxyquinoline chelating ion exchangers for their behavior toward aluminum. Merritt and Walker (*7*) first reported that 2-methyl-8-hydroxyquinoline (8-hydroxyquinaldine) did not precipitate aluminum, a fact which they attributed to the small size of aluminum and the large size of the ligands. Irving et al. (*8*), commenting upon the ligand's failure to form 3:1 complexes with aluminum, concluded that it was impossible to form 2:1 or 1:1 complex between aluminum and 8-hydroxyquinaldine. However, Dagnall et al. (*9*) have reported that aluminum can be extracted by the ligand to some extent, while Cardwell (*10*) has shown that tris (8-hydroxyquinaldinato) aluminum (III) can be precipitated by careful pH control.

This paper examines some of the aspects of metal chelation on oxine and on 8-hydroxyquinaldine ion-exchange resins, particularly the little explored field of metal–metal exchange on the resin between the ion exchanger fully loaded with one metal in contact with a solution containing a second metal capable of giving a metal–resin complex of greater or equal stability.

EXPERIMENTAL

Ion-Exchange Resin Preparation

Full details of the synthesis of an oxine ion-exchange resin have been given elsewhere (*2, 3*). The procedure will be outlined here for the two resins. 8-Hydroxyquinaldine was prepared by a modified Skraup reaction according to the method of Manske et al. (*11*). 8-Hydroxyquinoline or -quinaldine (0.2 mole) are triturated with sodium hydroxide and 0.5 *M* of formaldehyde as 40% formalin, the mixture is warmed and stirred until solution is effected, 0.1 mole of resorcinol is dissolved in sodium hydroxide solution, and the mixture is added to the ligand–formaldehyde solution. Sufficient water is added to give a water content of 70%, and then the resin mix is sealed into a glass tube and cured at 100°C for 60 hr. The resulting cured gel is ground, soaked in water, and sieved. After several days washing with dilute hydrochloric acid to remove soluble materials, the resin is washed with water, then with sodium acetate solution to convert it to the neutral form, and finally washed with deionized water. The resin is stored under water and must never be allowed to dry out.

Metal Capacity

The procedure for metal capacity determination has been described in detail in previous work (*6*, *12*). A 1 *M* sodium acetate solution which is 0.1 *M* in the metal ion whose capacity is to be determined is adjusted to the selected pH by the addition of dilute sulfuric acid. Fifty milliliters of this solution is equilibrated with 0.5 g of fully swollen resin by shaking for 48 hr. After removal of resin and washing with buffer and then with deionized water, the sorbed metal ions are removed from the resin by equilibration with 2 *M* hydrochloric acid. The metal contents of the eluate are then determined. Atomic absorption spectrophotometry was used for all metal determinations described here.

Separation Ratios

Solutions of the chosen ion pairs were prepared, which were 0.1 *M* in each ion, in pH 4.0 acetate buffer. One hundred millilters of this solution was equilibrated with 0.5 g of fully swollen resin for 48 hr. After the washing and elution procedure described above, the concentrations of the two metals in the acid eluate were determined.

Metal-Metal Exchange

Metal loading of the resin was accomplished by shaking the resin with a large excess of 0.1 *M* zinc or aluminum solution in pH 4 acetate buffer for 48 hr. The resin was then filtered, washed with pH 4 buffer, and then with deionized water. One-half gram of this metal-loaded resin was equilibrated with various concentrations of the second metal solution in pH 4 buffer for 48 hr, larger volumes being used for the more dilute solutions. The resin was then filtered, washed thoroughly with buffer, and then with water. The two metals were then eluted using 2 *M* hydrochloric acid and their concentrations in the eluate determined.

Column Separations

The metal-loaded resins, prepared as described above, were packed into columns of 30 cm length in 50 ml burettes. After washing the column with five bed volumes of pH 4 buffer, 10 ml of sample solution containing 100 ppm of each metal ion (copper–aluminum or copper–zinc) in pH 4 buffer was passed through the column with a flow rate of 1 ml/min. After elution of the column with a further five bed volumes, the total column effluent was made up to volume and the concentrations of the two metals determined.

Water Regain

The resin, after equilibrating with deionized water for 48 hr, was filtered under slightly reduced pressure and then lightly pressed between sheets of filter paper to remove surface moisture. The moisture content of this fully swollen resin was determined by drying at 100°C for 48 hr, from which the water regain and hence the total capacities of the dry resin could be calculated.

RESULTS AND DISCUSSION

The total capacity vs pH contours given in Fig. 1 suggest certain separations, such as copper and iron from aluminum, zinc, cobalt, and nickel, which have proved feasible by column operation (*6*). The contours also suggest that the metal–resin stabilities are in the order Cu $\gg$ Al $=$ Zn, so it should be possible to retain copper quantitatively on either a zinc-loaded or aluminum-loaded resin. However, what would happen to aluminum on a zinc-loaded or zinc on an aluminum-loaded resin is not apparent. Separation ratios on the oxine exchanger, Table 1, confirm the finding that copper is preferred to zinc, and a separation ratio of 3.5 for Al/Zn indicates a preference for aluminum which is probably too small for column separation to be effected. Similar values for Al/Ni and Al/Co suggest difficulty in separating aluminum from these two metals also.

At pH 4.0 the metal capacities of the oxine exchanger for copper, aluminum, and zinc are 2.90, 1.05, and 1.25 moles/g, respectively. Table 2 shows the extent of metal–metal exchange on the zinc-loaded oxine resin at pH 4 when equilibrated with either copper solutions or aluminum solutions of various molarities. Table 3 shows a similar situation when the aluminum-loaded resin is equilibrated with either copper- or zinc-con-

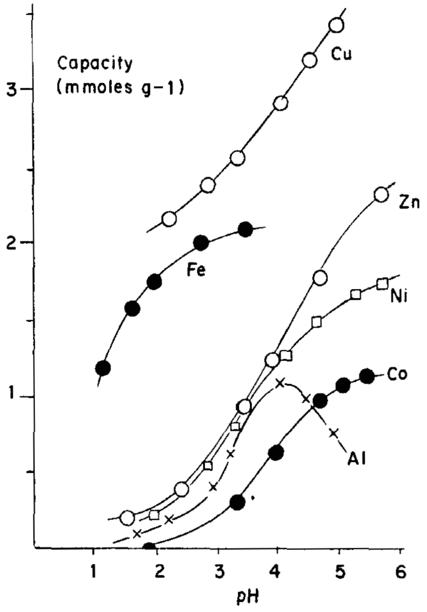

FIG. 1. Total capacity versus pH contours for an 8-hydroxyquinoline ion-exchange resin.

TABLE 1

Separation Ratios of Metal Ion Pairs with 8-Hydroxyquinoline and 8-Hydroxyquinaldine Resins (acetate buffer pH 4.0)

	Separation ratio				
Resin	$\frac{Al}{Zn}$	$\frac{Al}{Ni}$	$\frac{Al}{Co}$	$\frac{Ni}{Co}$	$\frac{Cu}{Zn}$
8-Hydroxyquinoline	3.5	3.3	3.0	6.5	49
8-Hydroxyquinaldine	0.3	0.8	0.5	—	—

TABLE 2

Zinc Form of Oxine Resin, Exchange with Copper and Aluminum at pH 4.0

Ion molarity in equilibrating solution		Ion capacity (mmoles/g)	Residual Zn capacity (mmole/g)	Total capacity
1.0	Cu	2.02	0.05	2.07
0.1	Cu	1.74	0.07	1.81
0.01	Cu	1.42	0.07	1.49
0.003	Cu	1.38	0.07	1.45
0.1	Al	0.78	0.36	1.14
0.01	Al	0.55	0.38	0.93
0.003	Al	0.42	0.38	0.80

TABLE 3

Aluminum Form of Oxine Resin, Exchange with Copper and Zinc at pH 4.0

Ion molarity in equilibrating solution		Ion capacity (mmoles/g)	Residual Al capacity (mmole/g)	Total capacity
1.0	Cu	2.22	0.07	2.29
0.1	Cu	1.84	0.12	1.96
0.01	Cu	1.41	0.17	1.58
0.003	Cu	1.30	0.17	1.47
1.0	Zn	0.99	0.35	1.34
0.1	Zn	0.67	0.54	1.21
0.01	Zn	0.36	0.55	0.91

taining solutions. The results clearly show how the extent of replacement of a metal on the resin by a second metal in solution is dependent on the concentration of that second metal, the capacity for the second metal decreasing markedly with decreasing concentration in solution in each of the four cases. The exchange is, however, a complicated process. If this process was simply metal–metal exchange on a 1:1 basis (as is generally accepted for the metal: resin complex), the values in the total capacity column would remain constant as these are the sums of the capacities for the two metals at pH 4. That they decrease with decreasing metal concentration in solution shows that the two processes—sorption and desorption occurring simultaneously—are each controlled by solution concentration and are not simple replacement reactions. Irrespective of whether the initial situation is an aluminum-loaded resin in contact with 0.01 *M* zinc ions or the reverse, at equilibrium the resin displays the greater capacity for aluminum (0.55 mmole/g) than for zinc (0.37 ± 0.01 mmole/g), and the relative metal contents are not in agreement with the separation ratio, given as 3.5. However, the routes to this apparently limiting case of metal–metal exchange are quite different. With 0.1 *M* metal solutions, the entering aluminum is able to occupy some 68% of available resin sites at pH 4 whereas zinc is only able to occupy 55% of the sites on the aluminum-loaded resin. It may be seen that it is only in the case of the zinc-loaded resin in contact with 0.1 *M* aluminum solution that the ratio of the two ions on the resin at equilibrium begins to approach the value given in Table 1 for the Al/Zn separation ratio of 3.5. An aluminum content in solution considerably in excess of 0.1 *M* would be needed to achieve the value.

With copper in the equilibrating solution, the situation is quite different and is that predicted from Fig. 1 data, namely that replacement of zinc or aluminum from the resin by copper ions is almost complete due to the much higher stability of the copper–resin complex. The extent of desorption of zinc or aluminum is essentially constant, but the sorption of copper ions is dependent on the copper concentration in solution.

Column Separations on Loaded Oxine Resin

Columns of zinc- and aluminum-loaded resins were examined for their separating efficiency as the results so far examined indicate that, at pH 4.0, an aluminum-loaded resin should quantitatively retain copper but may not retain zinc. On the aluminum-loaded resin, copper retention was indeed quantitative; however, 30% of the zinc was also retained. On a zinc-loaded resin, copper retention was also quantitative, and in this case 54% of the aluminum was retained. These relatively high retentions of the second metal are explained readily by the mechanics of column operation. The solution is continually meeting fresh metal-loaded resin, requiring a new equilibrium to be established. Even if this equilibrium favors aluminum–resin over zinc–resin complexation, with zinc ions continually meeting fresh aluminum-loaded resin, the zinc will be removed from solution.

8-Hydroxyquinaldine Resin

Table 4 gives the total capacities for copper, iron, and aluminum on the 8-hydroxyquinaldine exchanger and also on an oxine exchanger whose copper and iron capacities were very similar. This is not the oxine exchanger used in the other work carried out. Capacity vs pH contours are not given as these are very similar to Fig. 1 (the data for the oxine resin),

TABLE 4

Comparative Properties of the 8-Hydroxyquinaldine and an 8-Hydroxyquinoline Resin

Resin	Metal capacities			Water regain (g/g)	Equilibration rate ($t_{1/2}$ min)
	Cu, pH 5.0	Al, pH 4.0	Fe, pH 2.8		
8-Hydroxyquinaldine	3.4	0.5	1.4	1.5	13
8-Hydroxyquinoline	3.2	1.1	1.4	2.4	6.5

the main difference being the much lower capacity of the 8-hydroxyquinaldine resin for aluminum at its capacity maximum at pH 4.0. The shapes of the aluminum–resin capacity vs pH curves are identical, both having the pH 4.0 maximum. This is a strong indication that in the oxine resin, as in the 8-hydroxyquinaldine resin, aluminum–resin complexes are 1:1. Due to the steric hindrance of the 2-methyl group, it could be that aluminum–resin stability is considerably lower than for oxine in a similar manner to the lowering of stability constants of 1:1 and 2:1 complexes of copper with oxine by the presence of the 2-methyl group in copper-8-hydroxyquinaldine complexes (*13*, *14*). Table 1 gives the separation ratios for aluminum with zinc, cobalt, and nickel on the 8-hydroxyquinaldine exchanger and, by comparison with the oxine results, it is clear that the quinaldine resin selectively excludes aluminum.

The use of this exchanger in metal–metal exchange for the separation of copper and aluminum on a zinc-loaded resin should give more efficient separation than would the oxine resin. In fact, on the zinc-loaded resin copper was selectively retained while 9% of the aluminum present in the solution was also retained. This is a significant improvement over oxine which, in similar circumstances, retained 54% of the aluminum.

Metal–metal chelating ion exchange is an interesting theoretical phenomenon but is unlikely to find practical application as the large differences in metal–resin stabilities required to effect efficient separations render these amenable to pH control. Thus copper can be selectively separated from aluminum and zinc using a pH value of 2.8. The production of a sterically hindered chelating resin containing 8-hydroxyquinaldine has demonstrated that solvent extraction data gives much information about chelating ion exchange with the same ligand, aluminum being excluded by the resin. Metal–metal exchange is not a simple 1 for 1 exchange process, and further examination of this process could lead to a better understanding of the mechanism of chelating ion-exchange processes in general.

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