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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.

Interest in the use of 8-hydroxyquinoline (oxine) as an ion-exchange material has been sustained from the time Erlenmeyer and Dahn (*1*) attempted separations on columns of powdered oxine. Meinhardt (*2*) suggested absorbing the oxine on an inert support for column operation. This suggestion was followed by Andreev and co-workers (*3*) who have described the concentration of elements from ultradilute solutions using columns of active carbon impregnated with various complexing ligands, one of which was oxine. Yamamoto and Hiraoka (*4*) have used columns of oxine on cellulose for the separation of Hg(II), Co(II), Cu(II), and Fe(III). Chelating ion-exchange resins—where the oxine is chemically bonded to a cross-linked polymer matrix—have been developed and their chelating properties described recently (*5*, *6*). The development of the technique of extraction chromatography, by which separations are achieved on columns of supports impregnated with liquid chelating ligands (*7*), dates from the early 1960s and has been covered extensively by Braun and Ghersini (*8*). However, the column performance of oxine is poor due to the fact that it is a crystalline solid which is appreciably soluble in acid solutions. The first liquid ion exchanger incorporating oxine functionality was 7-dodecenyl-8-hydroxyquinoline, marketed by Ashland Chemicals under the name of Kelex 100. This reagent was developed for the solvent extraction of copper from acidic leach liquors, and its application to this field has been described by Ritcey (*9*). The use of Kelex 100 impregnated polystyrene bead columns for iron, copper, cobalt, and nickel separations has been described by the author (*10*).

The development of General Mills' LIX range of α-hydroxyoxime liquid ion exchangers as copper selective extractants (*11*, *12*) and the work of Parrish (*13*) on alkyl derivatives of salicylaldoxime made available liquid *o*-hydroxyphenoximes as chelating ligands. Cerrai and Ghersini (*14*) used LIX 64, a mixture of aliphatic and aromatic α-hydroxyoximes, on cellulose powder columns for the selective extraction of copper, and the author (*10*) has evaluated LIX 63 (an aliphatic α-hydroxyoxime) and LIX 65N (an *o*-hydroxybenzophenoxime) separately as impregnates on polystyrene beads for their copper selectivity. The whole field of copper hydrometallurgy using LIX and Kelex reagents has been extensively reviewed by Flett (*15*). Shortcomings of the reagents as impregnates on polystyrene beads were very low total capacity and slow equilibration rates, the ion-exchange behavior of the bead impregnates being found to be intermediate between chelating ion-exchange resins containing the same functional group and the reagents when used in solvent extraction. The development of solid foams as column support materials (*16*) has meant that fast equilibration rates of the LIX and Kelex reagents as foam impregnates could be achieved; their behavior therefore should resemble the solvent extraction mode of operation rather than the chelating ion-exchange mode. Relatively short impregnated foam columns could therefore be selective, quantitative collectors of ionic species from very dilute solutions and, as such, could prove to be of value in water and effluent analysis at trace levels. It is these aspects which are examined here; foam selectivities are evaluated in terms of separation ratios, copper recoveries from acid solutions are examined, and the two reagents are compared for their abilities to retain 10 ionic species (at ppm concentrations) from neutral solution.

EXPERIMENTAL

Reagents and Column Packings

LIX 65N, an alkyl β-hydroxybenzophenone oxime 50% solution in kerosene (General Mills Inc.), was dissolved in an equal volume of chloroform. The polyurethane foam was impregnated with this solution, excess reagent solution was squeezed out, and then the chloroform was removed under vacuum. Kelex 100, a 7-dodecenyl 8-hydroxyquinoline (Ashland Chemical Co.), was dissolved in three times its volume of chloroform. The foam impregnation and solvent removal procedures were as for LIX 65N. Stationary phase loadings were determined by the foams' increase in weight. After solvent removal, the foams were cut into small pieces (cubes of 3 to 5 mm side), and the foam columns (25 × 1 cm diameter) were prepared by vacuum packing (*15*).

Total foam capacities, foam kinetics, and separation ratios were obtained by batch equilibrations on 0.3 to 0.4 g samples of impregnated foams (*6*, *17*, *18*).

Metal Recoveries from Acidic Leach Liquor. The synthetic leach liquor, containing the metals listed at the concentrations given in Table 3, was a solution in 1 g/l sulfuric acid and had a pH of 2.0. After aliquots of solution had been passed through the columns, the retained metals were eluted with 2 *M* sulfuric acid and their contents determined. The percentage recovery of each metal from the leach liquor was then calculated.

Retention and Elution of Ten Metals at Trace Levels

The sample solution was prepared by diluting a standard solution of cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, uranium, and zinc (containing 100 ppm of each metal in 0.01 *M* hydrochloric acid) to 10 ppm in each and adjusting the pH to 6.0 by the addition of sodium acetate solution. At this pH some precipitation occurred; the solution was left to stand overnight, then the precipitate was removed by filtration immediately before the solution was to be applied to the columns. Samples of the filtrate were also retained for analysis.

Analysis of all metal solutions was carried out using an IL 351 atomic absorption spectrophotometer with the exception of uranium which was determined colorimetrically with oxine (*19*). The filtered metal solution at pH 6 contained 1.4 ppm chromium, 5 ppm copper, 2 ppm zinc, 10 ppm each of cadmium, cobalt, manganese, nickel, lead, and uranium, and 9 ppm of mercury.

RESULTS AND DISCUSSION

The total foam capacities for copper at pH 4 were L1X 14.3 mg/g and Kelex 25.1 mg/g. The L1X foam was 23.5% w/w loaded with a 50% solution of L1X 65N in kerosene, so the total capacity found means a copper to ligand molar ratio of 1: 1.95 at saturation. The ligand molecules are, therefore, all available for bonding with the formation of a 1:2 metal: ligand complex. On the Kelex foam, with a 33.3% Kelex loading, the total copper capacity represents a metal: ligand molar ratio of 1: 2.7. This means that either roughly 25% of the Kelex is not available for chelation due to overcrowding, or that the Kelex 100 sample is not pure 7-dodecenyl-8-hydroxyquinoline and contains some nonchelating diluent; the latter explanation seeming more likely.

Figure 1 shows how the foam capacities vary with time, both foams having far higher capacities for copper than for iron(III). The much faster equilibration rates with copper solutions over iron(III) solutions are revealed with the times to half equilibration, $t_{\frac{1}{2}}$, for copper being 1.25 and 0.25 min for L1X and Kelex, respectively, while the comparable values for iron(III) are 4.5 and 3.25 min, respectively. The competitive sorption characteristics of the two foams were studied with equimolar copper and iron solutions, and the extents of the preferential uptake of copper over iron at various pH values are shown in Table 1 as the Cu/Fe separation ratio of each foam. These separation ratios are of the order of 50:1 and are seen to increase with increasing pH over the range 1.5 to 3. The values for the two foams at a particular pH are very similar, in agreement with the equilibrium data seen in Fig. 1. As both L1X and Kelex will complex with copper and iron, it would appear that copper selectivity with both ligands is mainly dependent on a kinetic effect. Table 2 gives the foam selectivities for other metal pairs at pH 4 and, again, similarity in behavior can be observed. Neither foam has high selectivity for copper over nickel but both display selectivity for copper over zinc and also for uranium over vanadium.

Foam columns were used to treat a synthetic acid leach liquor containing iron, copper, cobalt, nickel, and uranium, the efficiency with which the foams stripped the metals from the liquor and were themselves stripped of the metals by acid washing being determined. Table 3 gives the initial concentrations of the metals in the leach liquor and lists the percentage of

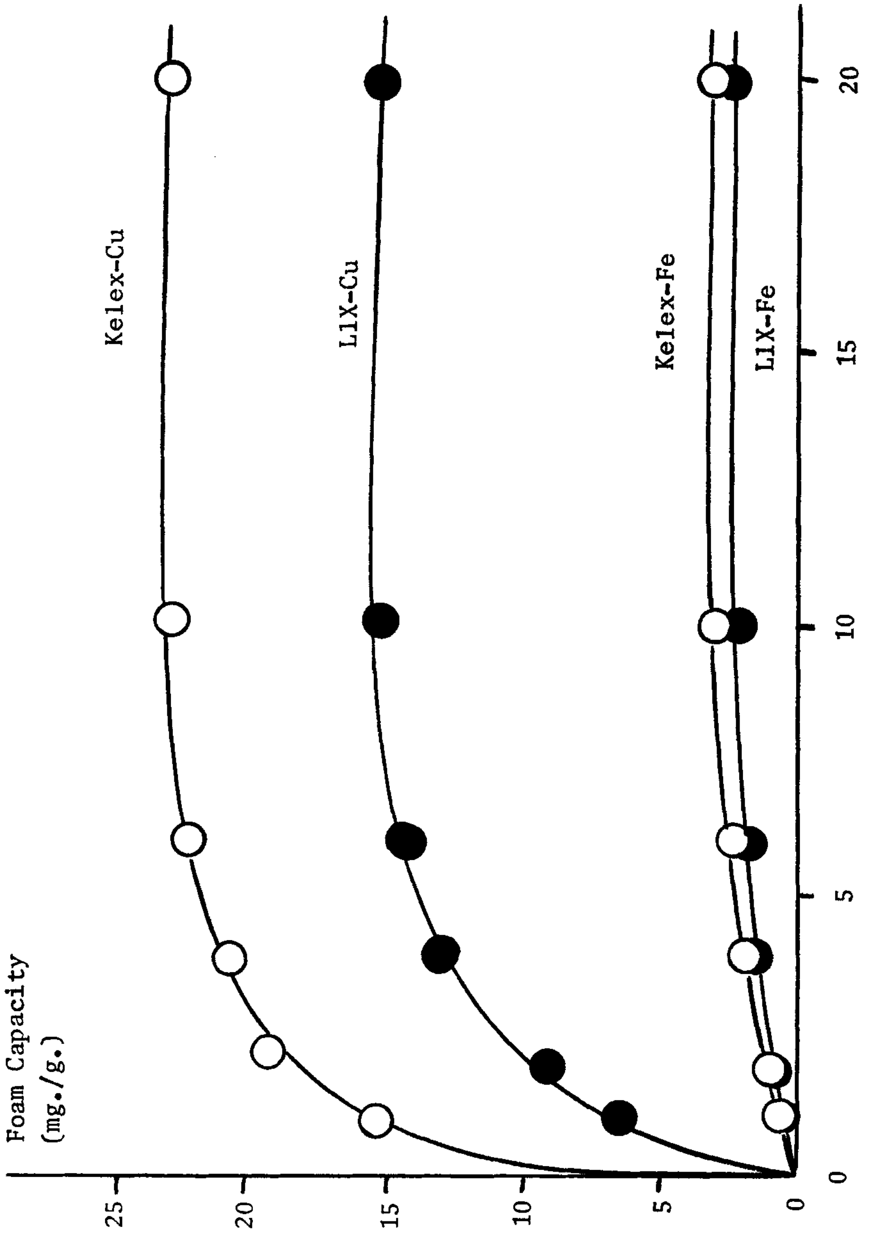

FIG. 1. Equilibration rates of the L1X 65N and Kelex 100 impregnated foams with copper(II) and iron(III).

TABLE 1

Dependence on pH of the Cu/Fe Separation Ratios on the Impregnated Foams

pH	Cu/Fe separation ratios	
	L1X 65N	Kelex 100
1.5	41	43
2.0	46	48
2.5	47	48
3.0	50	53

TABLE 2

Separation Ratios on the Impregnated Foams at pH 4.0

Ion pair equilibrated	Separation ratio	
	L1X 65N	Kelex 100
Cu/Ni	9	6
Cu/Zn	35	47
U/V	42	39

TABLE 3

Percentage Recoveries of Metals from an Acidic Leach Liquor after Ion Exchange on Impregnated Foam Columns

Species present in acid leach liquor (pH 2)	Initial conc (g/l)	Percentage of metal recovered	
		L1X 65N	Kelex 100
Fe	0.5	56	80
Cu	0.7	69	86
Co	0.2	9	20
Ni	0.2	8	14
U	0.2	84	88
H_2SO_4	1.0		

TABLE 4

Retention of Various Metal Ions by the Foam Columns from pH 6 Solution Using an Elution Rate of 0.3 ml/min

	Percentages of metals retained by the column									
Column	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	U	Zn
L1X 65N	0	94.3	0	94.6	99.4	0	98.6	80	100	0
Kelex 100	98.3	97.5	0	100	100	71	97.2	96.6	100	100

each metal obtained in the acid eluate. The Kelex impregnated foam is seen to be more efficient for the recovery of all the metals tested. Separation of cobalt and nickel from the other metals is indicated for each column.

A solution containing 10 trace metals was buffered to pH 6 and passed through each foam column slowly (0.3 ml/min) to assess each foam's extraction capability. Percentages of the metals retained by the foams are shown in Table 4, and it is found that the L1X 65N impregnated foam is the more selective, not retaining cadmium, manganese, chromium, or zinc, and having a more efficient retention for nickel. The Kelex 100 foam is a blanket extractant, retaining all but chromium and retaining cobalt, copper, mercury, and lead more efficiently than the L1X foam.

Using elution rates higher by a factor of 10 (3 ml/min), an attempt was made to separate the metal ions based on kinetic differences in complex formation and on differences in stability of the metal complexes formed. With a 3 ml/min elution rate, the solution-foam contact time was 5 min. Sorption onto the foam was followed by stepwise elution employing eluents of increasing acidity. The percentages of the metals in the column effluents and in the acid eluents are shown in Table 5. The only metal removed by the L1X foam with high efficiency was uranium whereas the Kelex foam was able to quantitatively remove mercury, lead, uranium, and zinc at pH 6. Differences in complex stabilities enabled the uranium to be removed from the L1X foam by pH 4 buffer whereas 0.1 *M* hydrochloric acid was necessary to elute it from the Kelex foams. For cobalt–nickel separation the results indicate that Kelex impregnated foam would be the more efficient, the cobalt being eluted with pH 4 buffer whereas 66 % of the nickel was retained by the column under these conditions. With the exception of mercury, which could not be removed from the Kelex column, efficient recoveries from the columns of all other elements were found.

Polyurethane foam is obviously not a support material which lends

TABLE 5

Elution Characteristics of Various Metal Ions on Impregnated Foam Columns with an Elution Rate of 3 ml/min

Eluting medium	Percentages of metals eluted									
	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	U	Zn
				From L1X 65N						
Column effluent (pH 6)	60	47	68	54	12	64	24	28	3	41
pH 4 buffer	36	42	29	15	15	32	36	62	80	42
0.1 *M* HCl	2	5	2	9	6	3	30	6	12	9
2 *M* HCl	2	6	1	22	35	1	10	4	5	8
				From Kelex 100						
Column effluent (pH 6)	10	2	75	20	0	65	7	1	0	1
pH 4 buffer	65	87	21	11	0	19	27	73	2	47
0.1 *M* HCl	20	5	3	20	4	5	36	18	64	40
2 *M* HCl	5	6	1	49	15	11	30	8	34	12

itself to the production of high efficiency columns with low HETP values and is not, therefore, suitable for column chromatography separations of metals. Its main advantage lies in the fact that high percentage coatings with a chelating liquid give rise to a column packing with very fast equilibration rates and hence efficient removal of metals from aqueous solutions. pH control of the sample solution could be employed to improve selectivity, and impregnated foam columns offer a method of collecting certain metal species from aqueous solutions which can be applied to such fields as environmental and effluent analysis and the production of metal-free solutions.

SUMMARY

Two commercially available liquid extractants, L1X 65N (an *o*-hydroxybenzophenone oxime) and Kelex 100 (7-dodecenyl-8-hydroxyquinoline) have been examined as column packings on a polyurethane foam support for their metal retaining abilities.

On this support, very favorable kinetics mean rapid equilibration with aqueous solutions. Sorption–desorption studies on 10 metal ions revealed that while L1X 65N was the more selective, the Kelex 100 column was the

more efficient system for the uptake of metals. Stepwise elution was examined for selective desorption, and foam selectivity is discussed in terms of kinetics of ion uptake and of separation ratios determined for several ion pairs.

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