Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Green, B. R. and Hancock, R. D.(1980) 'Diluent-Modified Impregnates for the Selective Extraction of Copper', Separation Science and Technology, 15: 5, 1229 — 1241
To link to this Article: DOI: 10.1080/01496398008066968
URL: http://dx.doi.org/10.1080/01496398008066968

SEPARATION SCIENCE AND TECHNOLOGY, 15(5), pp. 1229–1241, 1980

Diluent-Modified Impregnates for the Selective Extraction of Copper

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Abstract

Inert diluents were included in resin impregnates of copper selective reagents to improve their selectivity for copper over iron(III). The modified impregnates performed similarly to conventional ones in other respects with the exception that the loading rates were generally slower. This is a problem that can be overcome to some extent by the correct combination of resin matrix, diluent, and reagent. However, there appears to be a trade-off between diluent loss and kinetics.

INTRODUCTION

Since the introduction of the Lix and Kelex copper extractants there have been a number of reports (*1–7*) relating to the use of these reagents in resin impregnates. The formulations were aimed at obtaining low cost reagents (compared to the conventional ion exchangers), analytical reagents, and resins that could be used as an alternative to solvent extraction for upgrading the metal values of dump leach liquors. The use of impregnates would not involve the loss of reagent through entrainment that is experienced in the solvent extraction process.

Presumably, it was intended that the impregnates should exhibit the same selectivity toward metals as the reagents in solvent extraction. In the earliest work by Warshawsky (*1*), one of the more important features of the Lix impregnate, its selectivity for copper over iron(III), was not mentioned. However, in later work (*7*) using Lix 64N, he reported a separation ratio of as much as 500. Hughes and Purdey (*2*) found in a column experiment that an impregnate of Lix 64N selectively absorbed copper over iron(III), but no details were given. Vernon and Eccles (*5*) reported a separation ratio of 12.6 and, more recently, 40 to 50 (*6*) on Lix 65N impregnates. Parrish (*3*), using a Kelex 100 impregnate, observed a quantitative absorption of iron(III) in a column experiment, although this was not in the presence of copper. A separation ratio for copper over iron(III) of 1 was reported by Vernon (*5*) on a Kelex 100 impregnate whereas, more recently (*6*), using a polyurethane foam support, ratios of between 43 and 53 were achieved.

It is common in extraction chromatography to use a diluent together with chelating agents. Parrish (*3*) believed that this should be unnecessary when a support with a large surface area is used, as in the instance of the XAD matrix, but he did observe an improved exchange rate in the presence of a diluent. Warshawsky, in his more recent work (*7*), added hydrophilic modifiers to impregnates and found that this improved the effectiveness of Lix-type reagents with respect to copper loading. He also used a "wet method" of impregnation in which the metal–ligand complex is formed in the presence of a residual amount of organic solvent. This is in contrast to the "dry method" in which excess solvent is removed under vacuum after impregnation (*1*). This also improved the performance of the resin. The effect of diluents, modifiers, or residual sovent on the selectivity of the impregnates was not mentioned by any of the authors.

There seemed to be little agreement among the various sets of results that had been published, and a study of the factors that determine selectivity in the impregnates was needed.

It is generally accepted (*8*, *9*) that the Lix and Kelex-type reagents owe their large selectivity to kinetic factors related to the interface reaction. For this reason our approach to the preparation of impregnates with these reagents differed from those previously reported. We added diluents to the resin impregnates in order to obtain the interface necessary for the production of an acceptable selectivity. The present work deals with the performance of impregnates prepared in this way.

EXPERIMENTAL

Reagents

Lix 65N was purified as described elsewhere (*10*). Lix 63 is a pure reagent obtained from General Mills Inc. Kelex 100 was purified from the commercial reagent by column chromatography. BNN, containing a nitrosonaphthol group, is a pure compound that was synthesized at the National Institute for Metallurgy (NIM).

Diluents

Perchloroethylene, α-bromonaphthalene, Solvesso 100, and Solvesso

150 are commercial grade solvents. Solvesso 100 was brominated as follows: 40 mL of bromine was added dropwise to 50 g of Solvesso 100 that contained 0.5 mL of pyridine. When the reaction ceased, the mixture was heated to 70°C, at which temperature it was maintained for 2 hr. It was then cooled and filtered. The filtrate was washed with water, a 0.1 *M* sodium hydroxide solution, and then water until the pH was neutral. It was dried over calcium chloride.

Resin Matrices

For conventional impregnates a Rohm and Haas XAD-2 resin was used, and a Rohm and Haas experimental matrix, XE-305, was chosen for the diluent-modified impregnates.

Formulation of Impregnates

For the preparation of a conventional impregnate a solution containing the reagent mixture in methylene chloride was slowly concentrated in the presence of a resin matrix on a rotary evaporator. The impregnate so formed was dried further under vacuum for 16 hr. When a diluent-modified impregnate was required, the diluent was added dropwise to an impregnate, prepared as described above. The impregnate was shaken as the diluent was added so that there would be an even distribution of diluent over the resin. The diluent-modified impregnate was shaken for a further 20 hr in a sealed flask before being loaded. Details of the impregnates used are summarized in Table 1.

Loading Rate Tests

Portions of the resin, each of 1 g, were contacted for various times with 50 mL of an artificial pregnant solution. The resin was stirred throughout the contacting. The loaded resins were washed with water and eluted completely with sulfuric acid (120 g/L). The copper and iron contents of the eluent were determined by atomic absorption spectroscopy. Separation ratios according to the formula

$$\alpha_{\mathrm{Cu}^{2+}/\mathrm{Fe}^{3+}} = \frac{[\overline{\mathrm{Cu}^{2+}}][\mathrm{Fe}^{3+}]}{[\mathrm{Cu}^{2+}][\overline{\mathrm{Fe}^{3+}}]}$$

were calculated from these results.

Artificial Pregnant Solutions

The solutions had the following compositions.

TABLE 1

Formulation of Impregnates

	Matrix (g)		Reagent (g)				Diluent (g)		
Resin no.	XAD-2	XE-305	Lix 65	Lix 63	Kelex 100	BNN	Perchloroethylene	Bromonaphthalene	Brominated Solvesso 100
1	5.00		2.00	0.08					
2	5.00				2.00				
3		4.20	1.50	0.06			7.00		
4		2.60			1.33		4.06		
5		2.10	1.00			0.13	3.25		
6		2.10	1.00			0.13		3.25	
7		2.10	1.00			0.13			3.25
8		2.10				0.81			3.25
9		2.10	1.17	0.05					3.25
10		2.10	1.00			0.13			1.63
11		2.10	1.00			0.13			4.88
12		2.10	1.50			0.20			4.88
13	4.2		1.50	0.06			7.00		

Sulfate medium: 1 g/L of copper, 3 g/L of iron(III), and 10 g/L of magnesium, as sulfates. The solution was saturated with calcium sulfate and the pH was adjusted to 2 with sulfuric acid.

Nitrate medium: 1 g/L of copper and 1 g/L of iron(III) as nitrates. The pH was adjusted to 2 with nitric acid.

"Equilibrium" Curve

Portions of Impregnate 5, each of 1 g, were contacted for 5 hr, while stirring, with 50 mL of solution containing different quantities of copper and 3 g/L of iron(III), 10 g/L of magnesium, and with a pH of 2. Loaded resins were eluted completely with sulfuric acid (120 g/L), and the metal values in the eluate and depleted solutions were determined by atomic absorption spectroscopy.

Solvent Losses

Impregnates (20 mL, fluidized) were contacted with water (25 L, recirculated at about 100 mL/min) in a pulsed column until it became apparent from the change in the resin-bed volume that solvent was being lost. When the experiment time exceeded 24 hr, the water was replaced. Solvent loss was estimated from the change in the resin-bed volume.

RESULTS AND DISCUSSION

So that the effect of an inert diluent on the selectivity of the resin could be determined, two types of impregnate were prepared. An XAD-2 matrix with a large surface area was employed in one case to obtain a conventional impregnate. The reagents were dried onto the resin from a volatile solvent which was then removed completely under high vacuum. XE-305 was chosen for the diluent-modified impregnates because of its good swelling ability. The reagents were impregnated in the usual way and an inert diluent, that swelled the resin, was added. Thus an impregnate bead can be likened to a droplet formed during mixing in solvent extraction, except that the bead is stable, being supported by a polymeric skeleton.

A comparison of the performance of the two types of impregnate is given in Figs. 1 and 2, and some data as to selectivity and kinetics are summarized in Table 2. When impregnates are loaded they rapidly attain a pseudo-equilibrium state dictated by kinetic factors. Thereafter, the quantity of various metals absorbed can slowly change as the true thermodynamic selectivity is approached. It is this pseudo-equilibrium that is

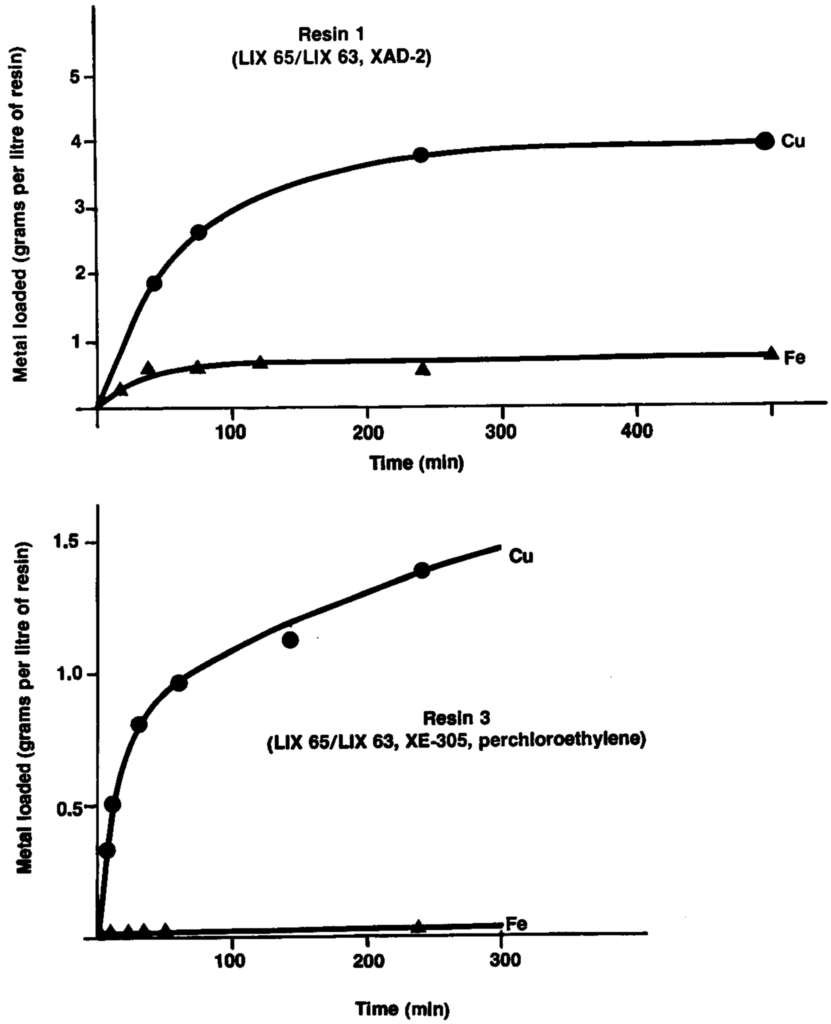

FIG. 1. The effect of diluent on loading on Lix impregnates.

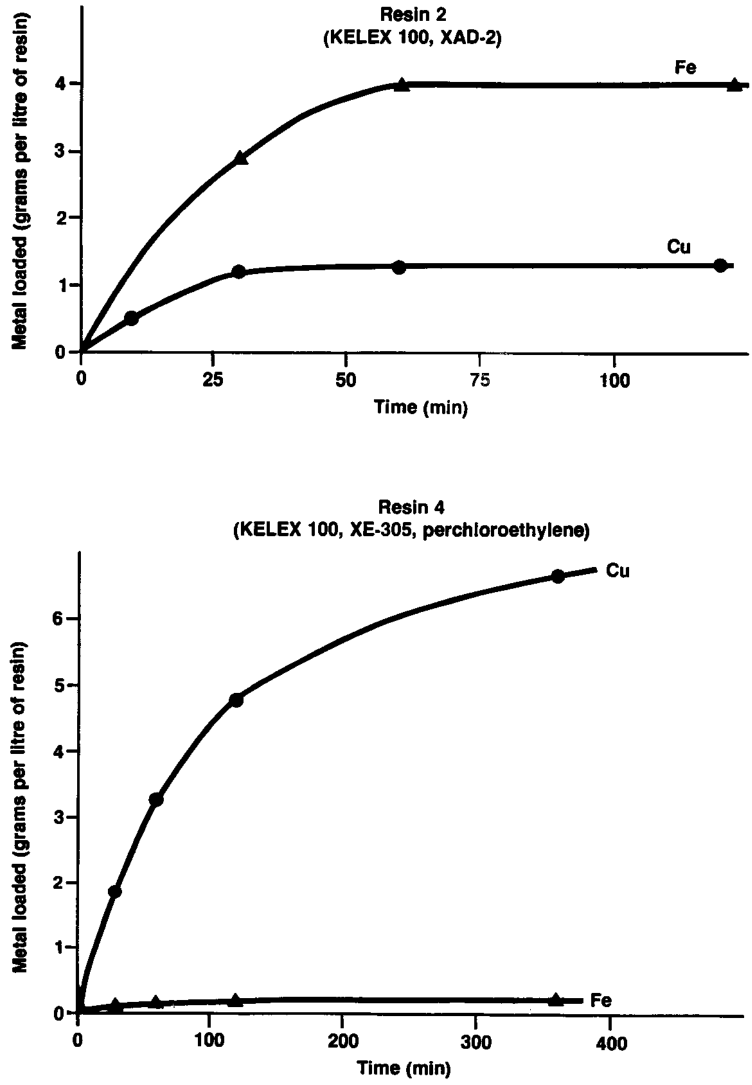

FIG. 2. The effect of diluent on loading on Kelex impregnates.

TABLE 2

Selectivity and Kinetic Properties of Lix and Kelex Impregnates

Resin	Type	$\alpha_{\mathrm{Cu/Fe}}$[a]	$t_{1/2}$[b]
1	Lix, XAD-2	13	45
3	Lix, XE-305, perchloroethylene	200	35
13	Lix, XAD-2, perchloroethylene	250	—
2	Kelex, XAD-2	0.1	15
4	Kelex, XE-305, perchloroethylene	70	70

[a] Separation factor at equilibrium copper loading or at the longest loading time where equilibrium had not been achieved.

[b] Time to 50% loading. When equilibrium was not achieved, a value for the equilibrium copper loading was estimated.

referred to in Table 2, and also in Fig. 7. The improvement to the selectivity for copper over iron(III) when a diluent has been used is quite clear for both the Lix and the Kelex reagents. In fact, in the instance of Kelex, a reversal of the selectivity is observed. This may explain the large discrepancies in the separation ratios that have been achieved previously with impregnates when this reagent was employed.

Vernon (*5*, *6*) mentioned the possibility of high-boiling paraffins or nonchelating diluents being present in his preparations. The amount of these substances remaining in the impregnated resin after vacuum treatment is uncertain, but it seems highly probable that, if they were present, they could have affected the selective properties of the resins. The same could be said for Lix impregnates whose reported selectivities (*5–7*) vary substantially.

In work reported here and elsewhere, a sulfate medium has often been employed during the loading of a resin because of its possible application in the treatment of dump leach liquors. The separation ratio obtained may not necessarily reflect the true selectivity, however, because competition between sulfate ions and the resin for iron(III) reduces the amount of this metal that is absorbed by the resin. This effect is illustrated by the results in Table 3 for Lix impregnates. Separation ratios are reduced substantially when loading takes place from nitrate media, in which no such competition between resin and solution species exists. The results for Resin 1 in a nitrate medium suggest that, even when an inert diluent is not present, a kinetic effect operates. The reagent, if it is not present as a monolayer, may be functioning as its own diluent.

One problem associated with the diluent-modified impregnates is that the inert solvent may be leached out during use. This would result in the loss of selectivity, and a deterioration of the performance of the resin. Perchloroethylene, the diluent used in the examples discussed so far, is

TABLE 3

Effect of Anionic Solution Species on the Observed Selectivity of Impregnates

Resin	Type	Anionic species	$\alpha_{Cu/Fe}$	Loading time (hr)
1	Lix, XAD-2	Sulfate	17	4
			17	24
			16	72
		Nitrate	9	4
			3	24
			1.7	168
3	Lix, XE-305, perchloroethylene	Sulfate	~200	4
		Nitrate	~70	4

TABLE 4

Loss of Diluent from Impregnates in Contact with Water

Diluent	Contact time (hr)	Diluent loss (%)
Perchloroethylene	8	70
Solvesso 150	24	17
α-Bromonaphthalene	40	13
Brominated Solvesso 100	70	0

lost rapidly. It is therefore necessary to find a more suitable substitute. Resins containing Solvesso 150, bromonaphthalene, and a brominated Solvesso 100 (which proved to be the best in this respect) were tested for loss of diluent. The results are summarized in Table 4. Furthermore, loading rates for impregnates employing some of these diluents (Resins 5, 6, and 7) were investigated. The results of these experiments, illustrated in in Fig. 3, indicate a deterioration of kinetics for impregnates containing brominated Solvesso 100 and bromonaphthalene. This is probably a diffusion problem, the result of the diluent being more viscous.

The loading rate of a diluent-modified impregnate is also dependent on the choice of reagent. Impregnates 7, 8, and 9 were prepared using the brominated Solvesso diluent, and different reagents and reagent mixtures. The total molar concentrations were kept similar. Loading rate curves are given in Fig. 4. An impregnate containing a copper-selective reagent (BNN) developed at NIM loaded about 50 times faster than a similar Lix 65/Lix 63 impregnate, whereas a 6: 1 reagent mixture of Lix 65 and BNN produced a loading rate 20 times faster than Lix 65/Lix 63.

The relative quantities of matrix, reagent, and diluent in an impregnate may affect the loading rate significantly. The formulation of Resin 7 was altered to give impregnates with 50% of the diluent (Resin 10), 150% of the diluent (Resin 11), and 150% of the reagent and diluent (Resin 12).

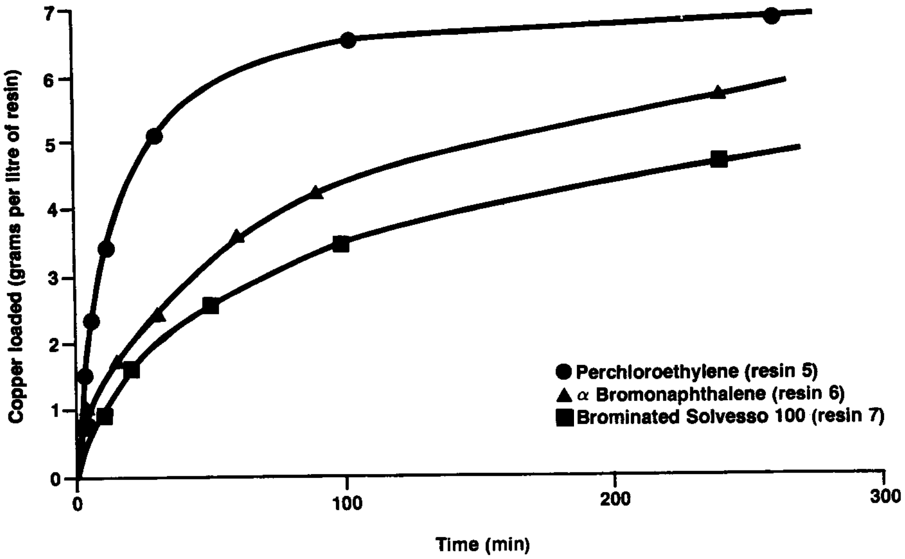

FIG. 3. The effect of diluent on loading rate.

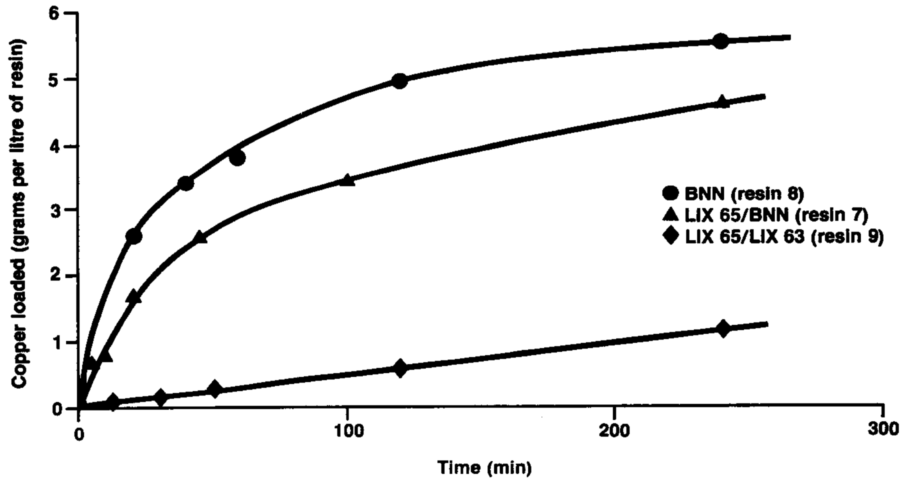

FIG. 4. The effect of reagent on loading rate.

A comparison of the loading rates of these impregnates is given in Fig. 5, and the results give forewarning of how the kinetics of an impregnate may be affected by the loss of diluent.

As can be expected, the loading rate can be improved dramatically by increasing the temperature at which the impregnate is contacted with the liquor. The results obtained by loading a Lix impregnate (Resin 9) at different temperatures are given in Fig. 6.

The equilibrium-distribution curve for copper was determined for

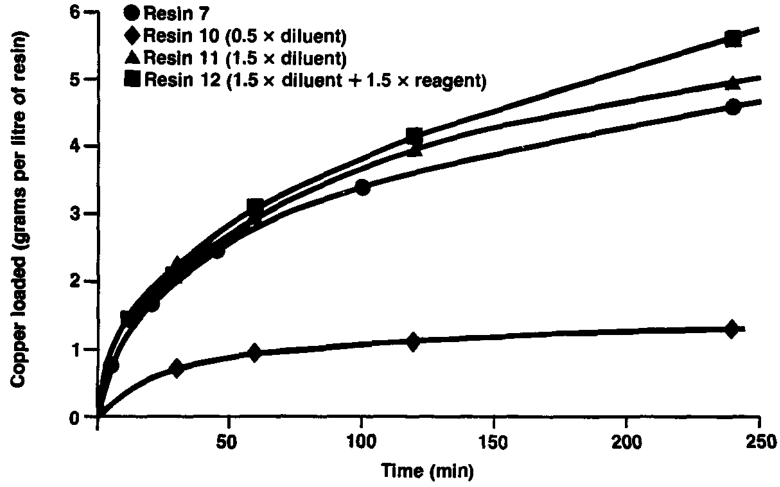

Fig. 5. The effect of the ratio of impregnate constituents on loading rate.

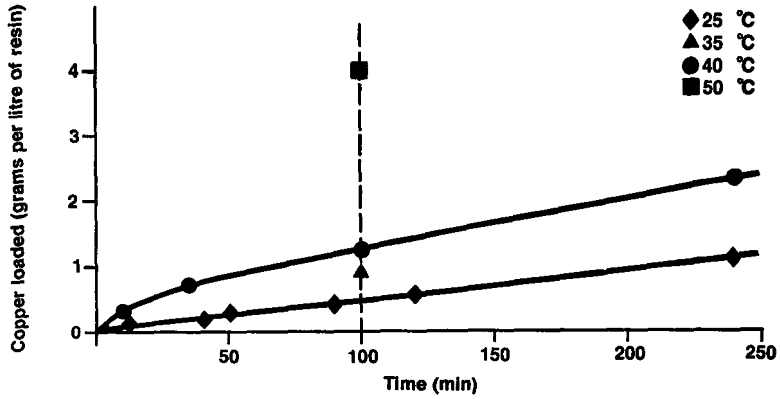

Fig. 6. The effect of temperature on loading rate.

Resin 5, an impregnate containing a 6:1 ratio of Lix 65 to BNN. The experiment was carried out in the presence of iron(III) maintained at a concentration of 3 g/L. The results are given in Fig. 7, and the amount of iron absorbed at various concentrations of copper is also plotted. Equilibrium curves for Lix and Kelex impregnates have been reported previously (*1*, *4*, *5*). An attractive property in the present case is the relatively high capacity which the impregnate exhibits for copper at low solution concentrations. For comparison, the equilibrium data of Whewell and Hughes (*11*) (for a 20 vol-% Lix 64N in Escaid 100 solution, with copper in 1 g/L sulfuric acid) are reproduced (broken line) in Fig. 7.

It is not easy for the performance of diluent-modified impregnates to be compared with previously reported results because of the differences in resin formulation and experimental details. However, capacities appear to be similar. Vernon (*12*) reported the column volumes required to retain 1 kg of copper when fully loaded as varying between 169 and 397 L, whereas typical values calculated for the present impregnates are 143 to 200. Separation ratios for copper over iron(III) have been given (*12*) as 4 to 48 and, in one case, approaching 500 (*7*). Vernon (*12*) expressed some doubt as to the validity of this high value for an impregnate when

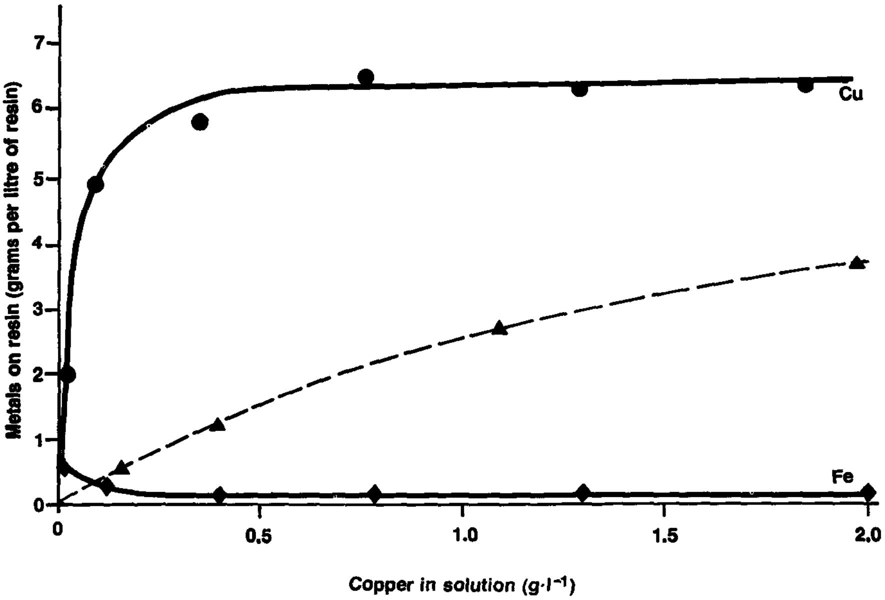

FIG. 7. Equililibrium data for copper on a Lix/BNN diluent-modified impregnate.

a limiting value of only 80 for Lix is obtained for solvent extraction. However, in the present case, separation factors of 200 were common and it has been confirmed (*13*) that this value, and probably even higher ones, should be possible for solvent extraction. Loading rates for the diluent-modified impregnates are generally not as good as those for impregnates prepared by Vernon (*12*) ($t_{1/2}$ = 0.25 to 11 min) and Warshawsky (*7*) ($t_{1/2}$ = 2 to 10 min). The best result obtained in the present case was $t_{1/2}$ = 10 min.

Acknowledgment

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Received by editor September 24, 1979