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Batch Extraction Studies of Cationic and Anionic Heavy Metallic Species by a Mixed Solvent Extraction System

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ABSTRACT

Removal of toxic heavy metals from wastewaters and their recovery is a challenging problem. Simultaneous and synergistic batch extraction from water of copper present as a cation (Cu^{2+}) and Cr^{6+} present as an anion ($HCr_2O_7^-$) into a mixed solvent extraction system have been studied. The mixed solvent extraction system consists of the diluent kerosene, the cation exchanger LIX 84, and trioctyl amine (TOA) which extracts anions via ion-pair formation with a proton. Highly efficient extraction has been achieved for both copper and chromium. Simultaneous extraction of two cations, Cu^{2+} and Zn^{2+}, as well as the anionic form of Cr^{6+}, ($HCr_2O_7^-$), has also been studied using mixtures of LIX 84, di-2-ethylhexyl phosphoric acid (D2EHPA), and TOA in the diluent kerosene. For an appropriate mixture composition, all three metallic ionic species can be simultaneously extracted with high efficiency. The extent of complexation between the basic extractant, TOA, and the acidic extractant/s is important in determining the extraction efficiency. A model developed for the extraction of Cu^{2+} using a mixed solvent extraction system provides a reasonable description of the observed extraction behavior and provides a first step for modeling.

INTRODUCTION

Electroplating, electronics, photographic, smelting, nuclear industries, etc. produce large volumes of dilute but hazardous waste streams containing a variety of heavy metals. In addition, surface and groundwaters in many places

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are similarly contaminated. Current treatment of heavy metal-contaminated industrial wastewaters often rely on precipitation creating a solid waste stream needing disposal. It would be most useful to recover these metals individually in a concentrated form for reuse at the location or elsewhere and simultaneously obtain treated water for reuse. Although many chemical, physical, and biological treatment technologies are available, they all have advantages and shortcomings.

Solvent extraction may be used to remove efficiently toxic heavy metals, e.g., Zn, Cu, Cr, Cd, Hg, etc., from effluents to environmentally acceptable levels and recycle these metals to the original processes (10, 13). Pilot-plant studies have been made (10), but no economic information is available. It is also widely employed in the separation of organic acids and purification of bioproducts, e.g., antibiotics, amino acids, peptides, etc.

Heavy metal-contaminated wastewaters often contain a mixture of different cations and anions. For example, Cu, Zn, Ni, etc. are present as cations whereas Cr(VI), Hg, Cd, etc. are commonly found as anions. To prevent pollution while achieving resource recovery/recycling, heavy metals have to be recovered individually from such waste streams and concentrated. Selective solvent extraction/concentration of individual heavy metals using metal-specific extractants is an attractive option.

Solvent extraction of one metal over another having the same ionic form in an aqueous waste stream by a given organic extractant is highly pH-dependent (13). Even the extraction of an individual metal depends strongly on the aqueous solution pH. If a heavy metal is present as a cation, it can be extracted by an organic acidic or chelating extractant present in an organic diluent (13). For example, copper can be successfully and selectively extracted using a chelating extractant like LIX 64, a liquid ion exchanger (represented as RH), in an organic diluent (9, 11):

$$2RH(org) + Cu^{2}(aq) \rightleftarrows R_2Cu(org) + 2H^+(aq) \qquad (1)$$

The heavy metal may be present as an anion. For example, in a highly acidic solution Cr(VI) will be primarily present as $HCr_2O_7^-$ (6). It can be extracted via ion-pair formation with a proton using a long-chain alkyl amine (say, a tertiary amine represented as R_3N):

$$HCr_2O_7^-(aq) + H^+(aq) + 2R_3N(org) \rightleftarrows (R_3NH)_2Cr_2O_7(org) \qquad (2)$$

Alternatively, if the feed aqueous solution is basic, Cr(VI) will be present primarily as CrO_4^{2-}. Then one can extract Cr(VI) from an aqueous solution of, say, Na_2CrO_4 by anion exchange with quaternary ammonium compounds (R_4NCl) like Aliquat 336 in a diluent:

$$2Na^+(aq) + CrO_4^{2-}(aq) + 2(R_4N)Cl \rightleftarrows 2Na^+(aq) + 2Cl^-(aq) + (R_4N)_2CrO_4(org) \qquad (3)$$

Such extractions of metal into an organic extractant present in a diluent have been carried out successfully and nondispersively using hollow fiber membrane extractors (12, 17). The principle of nondispersive membrane-based solvent extraction was established by Kiani et al. (7). Kim (8) also studied membrane extraction of metals; his system was not nondispersive due to a lack of appropriate pressure control between the two phases. Simultaneous backextraction of a metal into a very acidic stripping solution (for Cu^{2+}) or a very alkaline stripping solution [for Cr(VI)] has been successfully achieved in a hollow-fiber-contained liquid membrane (HFCLM) device in a stable fashion (5). In one of the studies mentioned above (17), the first phase involved determination of the distribution coefficient/equilibrium constant of each metal between the aqueous solution and the organic diluent having a suitable extracting agent. This was followed by the extraction of each heavy metal using a microporous hydrophobic hollow fiber module in separate experiments with the aqueous solution flowing on the tube side and the extracting solvent phase flowing countercurrently on the shell side.

In the extraction of copper, as the proton is released to the waste solution, the effective distribution coefficient m_i of copper between the organic extractant and the wastewater is reduced; this can significantly and—depending on the pH range—drastically reduce copper extraction efficiency (17). The same is true with Zn^{2+}, Ni^{2+}, etc.

If, however, a heavy metal present as an anion in the wastewater is simultaneously extracted into a basic amine-containing organic extractant via an ion-pair formation mechanism, the proton released by Reaction (1) will be consumed; the pH range in the wastewater may be controlled (15). An example of such a synergy is provided if Cr(VI), in the form of $HCrO_4^-$, say, is simultaneously extracted via the reaction

$$HCrO_4^-(aq) + H^+(aq) + 2R_3N(org) \rightleftarrows (R_3NH)_2CrO_4(org) \qquad (4)$$

which consumes the protons released by Reaction (1). It is important to recognize here that individual recovery of each of the metals, Cu(II) and Cr(VI), in this fashion requires that we have two separate organic streams, one containing an acidic/chelating extractant and the other containing a basic amine extractant, each contact the aqueous waste stream locally.

Yang et al. (16) went further and proposed a mixed solvent extraction system containing an acidic as well as a basic organic extractant in an organic diluent. Yang et al. (16) showed via a few batch-stirred solvent extraction studies that both cationic as well as anionic heavy metallic species could be simultaneously and efficiently extracted into the mixed extractant. Thus, it was no longer necessary to have separate organic extractant phases to extract cationic and anionic forms of heavy metal ions in a solution as was done by Yang et al. (15). They (16) also studied the backextraction (stripping) of each heavy metal into a separate and appropriate aqueous stripping solution consecutively. They (16) demonstrated further that backextraction was easier with the mixed extraction system. Perhaps this is due to the considerable competition for complexation between the specific extractant and the heavy metallic ionic species and the specific extractant and the other extractant of opposite extraction tendency.

In order to develop a membrane-based extraction system for a variety of mixed metals using a mixed solvent extractant, considerable knowledge of batch solvent extraction is needed for such systems. Yang et al. (16) employed only a particular value of the total mixed solvent molar concentration, namely, 0.156 M (= 0.078 LIX 84 + 0.078 M TOA) in their introductory studies. They employed LIX 84 and trioctyl amine (TOA) in kerosene. In the present study batch extraction experiments were done with aqueous feeds containing Cu^{2+} and Cr^{6+} and a range of total mixed extractant concentrations. This provided a broader perspective on the range of utility of such mixed extractants. Batch extraction experiments were also conducted with aqueous feeds containing Cu^{2+}, Zn^{2+}, and Cr^{6+} and a mixed extractant consisting of LIX 84, di-2-ethylhexyl phosphoric acid (D2EHPA), and TOA in kerosene. Preliminary modeling of Cu^{2+} extraction in a batch system of mixed extractants containing LIX 84 and TOA in kerosene has been carried out. The extent of complexation between the oxime of LIX 84 and TOA is unknown, yet it controls the availabilty of the free extractants which can extract metallic species.

To our knowledge, simultaneous extraction of two or three heavy metals present as cations and anions from an aqueous solution by a mixed solvent extraction system has not been explored before. Our first report is in Yang et al. (16). Mixtures of acidic and basic extractants were employed earlier by Grinstead et al. (4) to extract a neutral inorganic salt, e.g., NaCl, KCl, $MgCl_2$, $CaCl_2$ (single-salt systems); Eyal and Baniel (2) used a similar mixed extraction system to extract a mineral acid, H_2SO_4, HNO_3, H_3PO_4, or a carboxylic acid (e.g., citric acid). Eyal et al. (3) reviewed the extraction of metal salts by mixed solvent extraction systems. This last review illustrates two types of aqueous solutions when multiple salts are present in the feed: multiple salts having a common anion (e.g., Cl^-, NO_3^- or $SO_4^=$) with cation/cation selectivity being the focus; multiple salts having a common cation (Ca^{2+}, Zn^{2+}) with anion/anion selectivity being the focus.

Simplified Model for Batch Extraction of Cu^{2+} with LIX 84 and TOA in Kerosene

Batch extraction of Cu^{2+} with LIX 84 and TOA in kerosene was modeled assuming that the following chemical reactions take place in the system.

1) Extraction of Cu^{2+} by LIX 84:

$$Cu^{2+}(aq) + 2RH(org) \rightleftarrows R_2Cu(org) + 2H^+(aq) \tag{5}$$

where RH stands for LIX 84.
2) Extraction of H_2SO_4 by TOA:

$$2H^+(aq) + SO_4^{2-}(aq) + R_3N(org) \rightleftarrows (R_3N)H_2SO_4(org) \tag{6}$$

where R_3N stands for TOA.
3) Formation of LIX 84–TOA complex:

$$RH(org) + R_3N(org) \rightleftarrows (RH—R_3N)(org) \tag{7}$$

Mass balances on Cu^{2+}, SO_4^{2-}, H^+, R_3N, and RH respectively yield the following equations:

$$[Cu^{2+}] = [Cu^{2+}]_0 - [R_2Cu] \tag{8}$$

$$[SO_4^{2-}] = [SO_4^{2-}]_0 - [(R_3N)H_2SO_4] \tag{9}$$

$$[H^+] = [H^+]_0 + 2\{[Cu^{2+}]_0 - [Cu^{2+}]\} - 2\{[SO_4^{2-}]_0 - [SO_4^{2-}]\} \tag{10}$$

$$[R_3N] = [R_3N]_0 - [(R_3N)H_2SO_4] - [RH—R_3N] \tag{11}$$

$$[RH] = [RH]_0 - 2[R_2Cu] - [RH—R_3N] \tag{12}$$

where the subscript "0" indicates starting concentrations.

Using Eqs. (8) and (9), Eqs. (11) and (12) can be modified to

$$[R_3N] = [R_3N]_0 - ([SO_4^{2-}]_0 - [SO_4^{2-}]) - [RH—R_3N] \tag{13}$$

$$[RH] = [RH]_0 - 2([Cu^{2+}]_0 - [Cu^{2+}]) - [RH—R_3N] \tag{14}$$

Equilibrium constants for Reactions (5), (6), and (7) can be written in terms of their molar concentrations as

$$K_{Cu}^{eq} = \frac{[R_2Cu][H^+]^2}{[RH]^2[Cu^{2+}]} \tag{15}$$

$$K_{SO_4}^{eq} = \frac{[(R_3N)H_2SO_4]}{[H^+]^2[SO_4^{2-}][R_3N]} \tag{16}$$

$$K = \frac{[RH—R_3N]}{[R_3N][RH]} \tag{17}$$

Using Eqs. (8) and (9), Eqs. (15) and (16) can be modified to

$$K_{\mathrm{Cu}}^{\mathrm{eq}} = \frac{([\mathrm{Cu}^{2+}]_0 - [\mathrm{Cu}^{2+}])[\mathrm{H}^+]^2}{[\mathrm{RH}]^2[\mathrm{Cu}^{2+}]} \tag{18}$$

$$K_{\mathrm{SO_4}}^{\mathrm{eq}} = \frac{([\mathrm{SO_4^{2-}}]_0 - [\mathrm{SO_4^{2-}}])}{[\mathrm{H}^+]^2[\mathrm{SO_4^{2-}}][\mathrm{R_3N}]} \tag{19}$$

The equilibrium constant for extraction of copper by LIX 84 has been determined by a number of researchers (14, 17). Here, the value of $K_{\mathrm{Cu}}^{\mathrm{eq}}$ chosen was 1.7 (17). In the extraction of sulfuric acid by TOA, salts of many kinds form at varying ratios of initial concentrations of the two reactants (1, 19). In the present model it is being assumed that Reaction (6) is predominant, and the equilibrium constant was chosen to be 5×10^8 $(\mathrm{mol/L})^{-3}$ (18). Equations (10), (13), (14), (18), and (19) were solved simultaneously using the programs in MATHEMATICA (Version 2.1) assuming different values (100, 150, and 200) for K (equilibrium constant defined by Eq. 17).

EXPERIMENTAL

Chemicals Used

LIX 84 (anti-2-hydroxy-5-nonylacetophenone oxime) (Henkel, Tucson, AZ), tri-*n*-octylamine (TOA) (Fluka, Ronkonkoma, NY), and di-2-ethylhexyl phosphoric acid (D2EHPA) (Sigma, St Louis, MO) diluted in kerosene (Fisher Scientific, Springfield, NJ) were used as extractants for Cu^{2+}, Cr^{6+}, and Zn^{2+}, respectively. Copper sulfate ($\mathrm{CuSO_4 \cdot 5H_2O}$), potassium dichromate ($\mathrm{K_2Cr_2O_7}$), and zinc sulfate ($\mathrm{ZnSO_4 \cdot 7H_2O}$) (Fisher Scientific, Springfield, NJ) were used for preparing the feed solution. The pH of the feed solution was adjusted using 0.1 M $\mathrm{H_2SO_4}$ or 0.1 M NaOH.

Analytical

Thermo-Jarrel Model 12 Atomic Absorption Spectrophotometer (AAS) was used for measuring concentrations of Cu^{2+}, Cr^{6+}, and Zn^{2+} in the aqueous solutions using individual hollow cathode lamps and conventional flame conditions with a fuel (acetylene) to air ratio of 3:9. For measurement of Cu^{2+}, high concentrations were diluted to a linear calibration range of 1–40 mg/L; measurements were made at 216.5 nm with a slit width of 0.15 nm. The concentration measurement of chromium was similar to that of copper except that the linear calibration range was 1–20 mg/L, and the wavelength and the slit width used were 425.4 nm and 0.5 nm, respectively. For measurement of Zn^{2+}, high concentrations were diluted to a linear calibration range of 0–0.4 mg/L; measurements were made at a wavelength of 213.9 nm with a slit width of 1.0 nm. The pH of the aqueous phase was measured using a Corning pH meter (Model 250, relative accuracy = 0.001 pH error, Fisher Scientific, Springfield, NJ).

Batch Extraction/Backextraction Experiments

Copper–Chromium System

Extraction was carried out by stirring 20 mL of aqueous feed solution containing copper sulfate and potassium dichromate with 20 mL of solvent containing LIX 84 and TOA in kerosene for about 30 minutes. After separating the aqueous and organic phases, the loaded organic containing Cu^{2+} and Cr^{6+} was stirred with 20 mL of 0.1 M NaOH solution for about 30 minutes. After separation of the aqueous and organic phases, the organic phase containing mostly Cu^{2+} was stirred with 20 mL of 2 M H_2SO_4 for another 30 minutes. These experiments were carried out in a 150-mL beaker. The aqueous and organic phases were separated using a separating funnel. The pH of the raffinate phase was measured after every extraction.

Copper, Zinc, and Chromium System

The feed solution was made by dissolving copper sulfate, zinc sulfate, and potassium dichromate in deionized water. The organic extractant contained LIX 84, D2EHPA, and TOA in the diluent kerosene. The relative amounts of LIX 84, TOA, and D2EHPA were varied over a wide range; four different compositions were employed to cover this range.

Calculated Quantities

The distribution coefficient (m_i) for a particular metal between the aqueous phase and the mixed extractant is defined by

$$m_i = \frac{\text{concentration of the metal in the organic phase}}{\text{concentration of the metal in the aqueous phase}} \tag{20}$$

RESULTS AND DISCUSSION

Copper and Chromium System

Batch experiments were conducted with different concentrations of copper and chromium in the aqueous phase at three different mixed extractant concentrations containing LIX 84 and TOA in equimolar proportions. In all experiments the ratio of copper concentration to chromium concentration remained constant at 1.36:1. Distribution coefficients (m_i) for copper and chromium

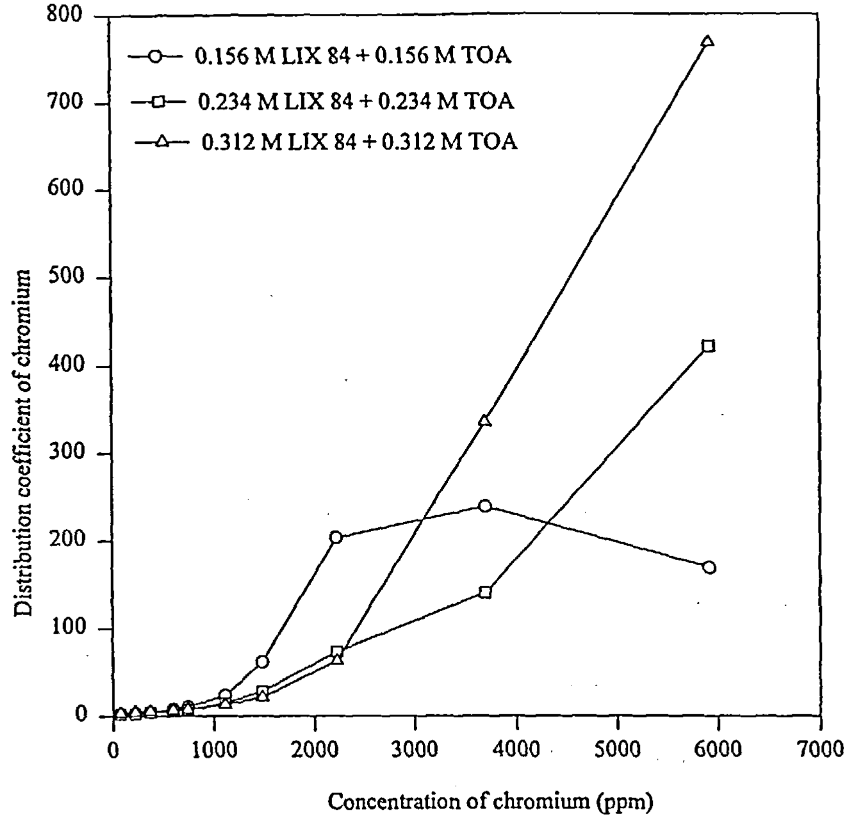

FIG. 1 Effect of feed concentration on the distribution coefficient of Cr(VI) at different mixed extractant concentrations in a batch extraction system.

were calculated after analyzing the aqueous raffinate phase using the atomic absorption spectrophotometer.

Figure 1 illustrates the variation of the distribution coefficient of chromium with concentration of chromium at three different mixed extractant concentrations. At low concentrations of chromium the distribution coefficient of chromium does not vary significantly as the mixed extractant concentration is increased. At a particular mixed extractant concentration of, say, 0.234 M LIX 84 + 0.234 M TOA in kerosene, the distribution coefficient of chromium increases with the concentration of chromium. At a lower mixed extractant concentration of, say, 0.156 M LIX 84 + 0.156 M TOA in kerosene, the distribution coefficient goes through a maximum and then decreases with an increasing concentration of chromium. At high concentrations of chromium the distribution coefficient of chromium increases very rapidly as the mixed extractant concentration is increased.

Figure 2 illustrates the variation of the distribution coefficient of copper with the concentration of copper at three different mixed extractant concentrations. The distribution coefficient of copper goes through a maximum and then decreases drastically as the concentration of copper increases. For example, at a copper concentration of 2020 ppm and a mixed extractant concentration of 0.312 M LIX 84 + 0.312 M TOA in kerosene, the distribution coefficient of copper was 10,100. At the same mixed extractant concentration, the distribution coefficient of copper dropped to 158 when the copper concentration

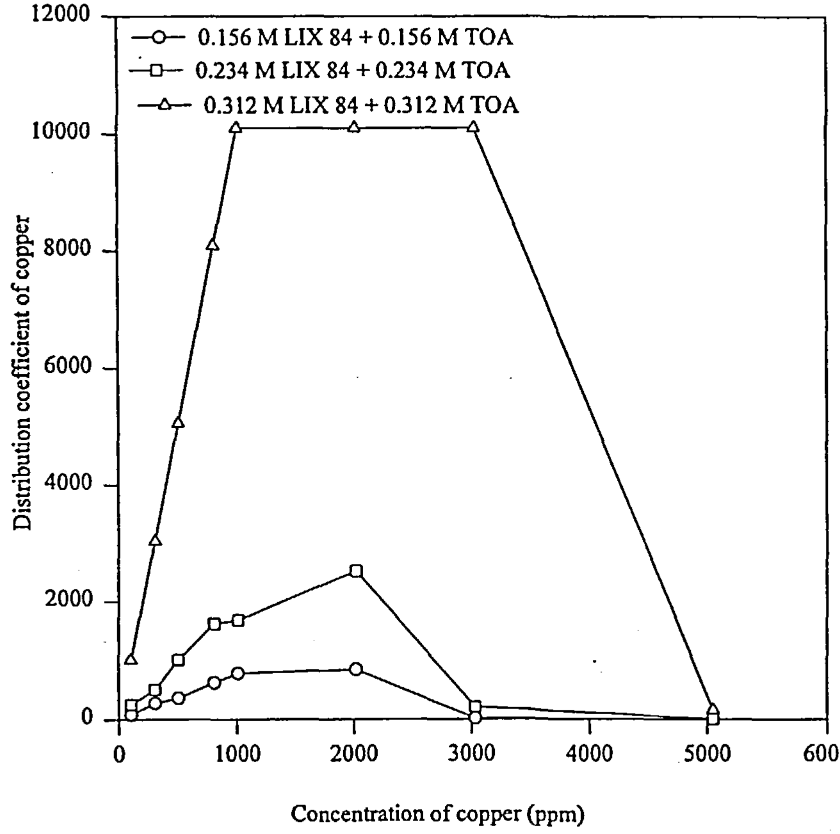

FIG. 2 Effect of feed concentration on the distribution coefficient of Cu(II) at different mixed extractant concentrations in a batch extraction system.

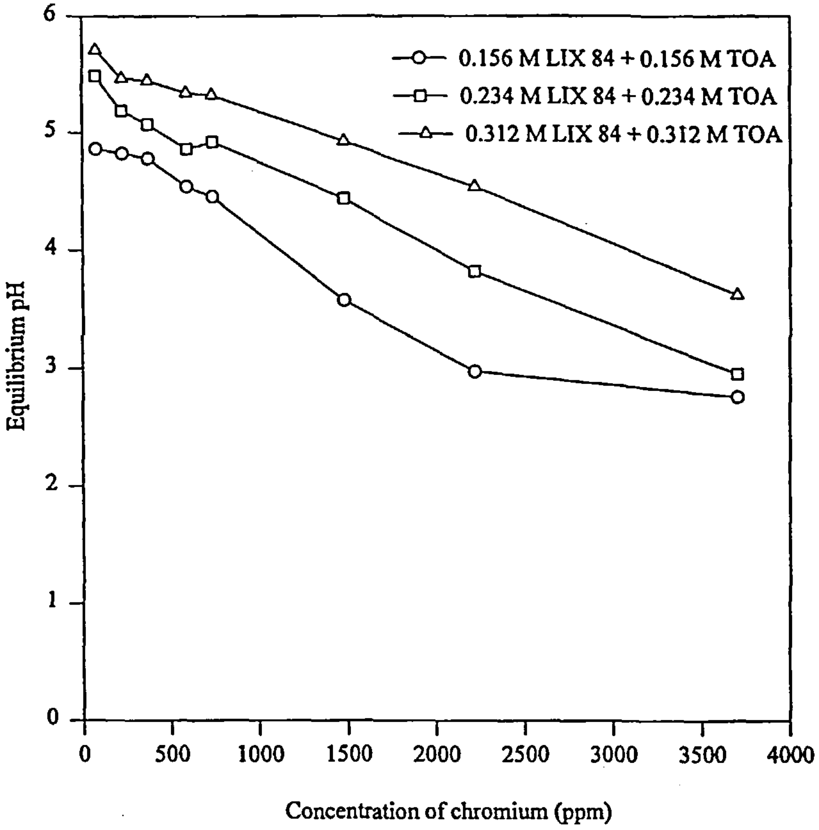

FIG. 3 *Effect of feed concentration on the equilibrium pH at different mixed extractant concentrations.*

was 5050 ppm. The distribution coefficient of copper increases drastically on increasing the mixed extractant concentration up to a certain concentration of copper. This concentration depends on the mixed extractant concentration: 2000 ppm for the two lower mixed extractant concentrations and 3000 ppm for the highest mixed extractant concentration.

Figure 3 illustrates the variation of the aqueous equilibrium pH with the metal concentration at three different mixed extractant concentrations. The starting aqueous phase was maintained at 4.0. At a particular mixed extractant concentration, the equilibrium pH decreases with increasing metal concentration. This can be explained as follows: When the concentration of copper in the feed is increased, more copper is extracted into the mixed extractant. This causes a large number of protons to be released into the aqueous phase. All the protons released are not used up in the extraction of chromium. At a particular metal concentration, as the mixed extractant concentration is increased, the aqueous equilibrium pH also increases. This is due to the fact that as the mixed extractant concentration increases, the metal extraction capacity and the distribution coefficient increase. Also, when the concentration of TOA is increased, more sulfate ions can be extracted, thus leading to a higher pH.

Figures 4, 5, and 6 illustrate the variation of the distribution coefficient of Cu(II) and Cr(VI) as the metal ion concentration is varied at mixed extractant concentrations, respectively, of 0.156 M LIX 84 + 0.156 M TOA in kerosene,

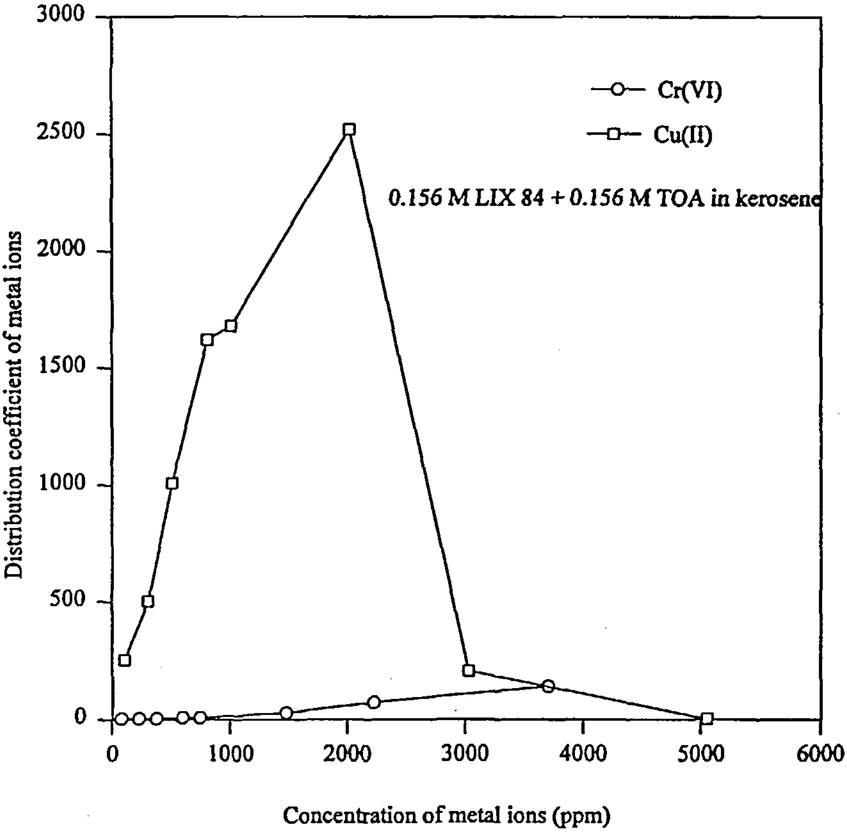

FIG. 4 Effect of feed concentration on the distribution coefficients of Cu(II) and Cr(VI).

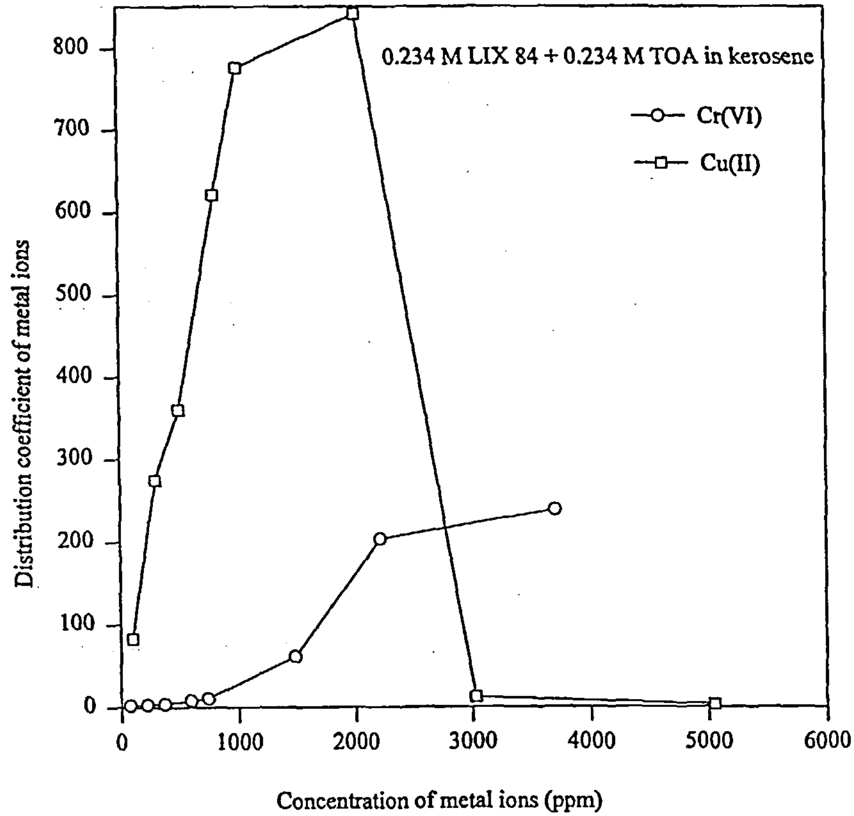

FIG. 5 Effect of feed concentration on the distribution coefficients of Cu(II) and Cr(VI).

0.234 M LIX 84 + 0.234 M TOA in kerosene, and 0.312 M LIX 84 + 0.312 M TOA in kerosene.

Copper, Zinc, and Chromium System

Batch extraction experiments were conducted with a mixed extractant containing different concentrations of LIX 84, TOA, and D2EHPA in kerosene. The feed concentration was kept constant at Cu(II) = 110 ppm, Zn(II) = 153 ppm, and Cr(VI) = 147 ppm for all experiments. The initial phase involved batch experiments to determine the optimum starting aqueous phase pH. Tables 1 to 7 show the experimental results for different compositions of the mixed extractant at different starting aqueous feed pH values. The results show that a feed pH of around 4.0 can be used for efficient extraction of the three metals.

At high concentrations of TOA, extraction of Cr(VI) is excellent but extraction of Zn(II) and Cu(II) is very poor (Table 1). This may be due to the fact that most of the LIX 84 and D2EHPA form a complex with TOA and thus lesser amounts of free LIX 84 and D2EHPA are available for extraction of Cu(II) and Zn(II). Since a high concentration of TOA is used, a significant amount of free TOA is left after complexation, thereby leading to a good extraction of Cr(VI). When a mixed extractant composition of 10% LIX 84, 10% D2EHPA, and 5% TOA in kerosene was used at a initial feed pH of 4.0, a reasonable extraction of all three metals could be achieved (Table 2).

A much lower raffinate pH of 2.43 was obtained when the mixed extractant composition was 10% LIX 84, 10% D2EHPA, and 5% TOA in kerosene (Table 2) compared to a raffinate pH of 4.083, which was obtained when the mixed extractant composition was 5% LIX 84, 5% D2EHPA, and 20% TOA

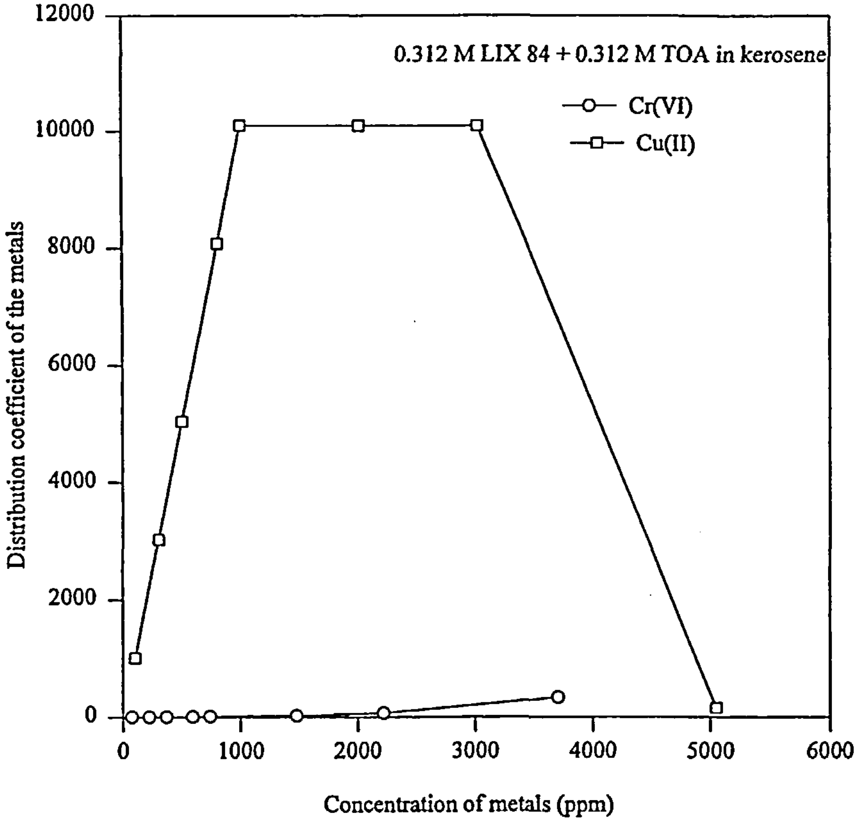

FIG. 6 Effect of feed concentration on the distribution coefficients of Cu(II) and Cr(VI).

TABLE 1
Batch Experimental Results for Copper, Zinc, and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 5%, TOA = 15%, D2EHPA = 5%

Initial pH	Raffinate pH	[Zn(II)] (ppm)	[Cu(II)] (ppm)	[Cr(VI)] (ppm)
2.5	3.101	125	36.50	0.49
3.0	3.478	101.5	7.09	0.15
3.5	3.613	91	3.42	0.26
4.0	3.716	72.5	1.88	0.22
4.4	3.72	90	2.2	0.31

in kerosene for the same feed concentration and same initial feed pH of 4.0 (Table 3). This is due to a greater extent of extraction of Cu(II) and Zn(II) by LIX 84 and D2EHPA at mixed extractant composition of 10% LIX 84, 10% D2EHPA, and 5% TOA in kerosene, which leads to the release of a higher number of protons (H^+). Table 4 shows the experimental results for a mixed extractant composition of 10% LIX 84, 10% D2EHPA, and 10% TOA in kerosene. Good extraction of chromium is obtained due to a higher concentration of free TOA.

Batch experiments were also done with a mixed extractant containing D2EHPA and TOA in kerosene for the three metal system at different feed pH. Results indicate that there was good extraction of Zn(II) and Cr(VI) but there was poor extraction of Cu(II) (Tables 5 and 6). This indicates that a mixed extractant containing D2EHPA and TOA in kerosene can be used for efficient removal of Zn(II) and Cr(II) simultaneously.

TABLE 2
Batch Experimental Results for Copper, Zinc, and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 10%, TOA = 5%, D2EHPA = 10%

Initial pH	Raffinate pH	[Zn(II)] (ppm)	[Cu(II)] (ppm)	[Cr(VI)] (ppm)
2.5	2.281	42.5	20	18.97
3.0	2.373	21.5	13.3	20.10
3.5	2.418	16	10.5	17.90
4.0	2.431	15	8.5	20.00
4.4	2.424	16	9.55	>20.00

TABLE 3
Batch Experimental Results for Copper, Zinc, and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 5%, TOA = 20%, D2EHPA = 5%

Initial pH	Raffinate pH	[Zn(II)] (ppm)	[Cu(II)] (ppm)	[Cr(VI)] (ppm)
2.5	3.200	126.50	>40	0.52
3.0	3.789	105.50	11.81	0.11
3.5	3.952	107.50	6.23	0.21
4.0	4.083	75.0	3.80	0.01
4.4	4.153	95.0	4.8	0.42

TABLE 4
Batch Experimental Results for Copper, Zinc, and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, LIX 84 = 10%, TOA = 10%, D2EHPA = 10%

Initial pH	Raffinate pH	[Zn(II)] (ppm)	[Cu(II)] (ppm)	[Cr(VI)] (ppm)
2.5	2.554	57.50	>40	0.95
3.0	2.684	36	31.50	0.68
3.5	2.714	31.50	25.88	0.40
4.0	2.758	25.5	26.47	0.69
4.4	2.769	29.50	24.86	0.45

TABLE 5
Batch Experimental Results for Copper, Zinc, and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, pH = 4.0, LIX 84 = 0%, TOA = 10%, D2EHPA = 20%

Initial pH	Raffinate pH	[Zn(II)] (ppm)	[Cu(II)] (ppm)	[Cr(VI)] (ppm)
2.5	2.289	14.0	86.40	1.0
3.0	2.421	6.0	76.0	0.29
3.5	2.466	5.5	76.4	1.0
4.0	2.478	6.5	74.80	0.49
4.4	2.502	4.0	72.0	1.16

TABLE 6
Batch Experimental Results for Copper, Zinc, and Chromium System with Cu(II) = 110 ppm, Zn(II) = 153 ppm, Cr(VI) = 147 ppm, pH = 4.0, LIX 84 = 0%, TOA = 5%, D2EHPA = 10%

Initial pH	Raffinate pH	[Zn(II)] (ppm)	[Cu(II)] (ppm)	[Cr(VI)] (ppm)
2.5	2.341	23.5	84.2	0.80
3.0	2.531	4.5	75.0	1.25
3.5	2.584	5.5	76.20	1.39
4.0	2.604	6.0	75.60	1.67
4.4	2.656	5.0	74.40	1.50

Table 7 summarizes batch experimental results for the three metal system at different mixed extractant compositions for a feed pH of 4.0 and the same feed concentration. Results show that a mixed extractant containing 15% LIX 84, 15% D2EHPA, and 5% TOA in kerosene provides the best metal-loading capacity. It can be seen that if one of the extractant concentrations in the mixed extractant is altered, extraction performance of all three metals is altered. This is due to a change in the concentration of the LIX 84–TOA and D2EHPA–TOA complexes when one extractant concentration is altered and thereby the concentrations of free LIX 84, D2EHPA, and TOA are altered.

We now consider the results of the simulations of the equilibrium batch extraction model developed earlier. Simultaneous simulation of Cu(II) and Cr(VI) is complicated by the lack of equilibrium data on Cr(VI) extraction. We therefore focused only on Cu(II) extraction. Simulations of Eqs. (10), (13), (14), (18), and (19) for a K value of 150 gave the best results, i.e., the calculated equilibrium concentrations of various species were close to the

TABLE 7
Batch Experimental Results for Copper, Zinc, and Chromium System at Different Mixed Extractant Concentrations at a Feed pH of 4.0

Organic composition			Feed composition			Raffinate composition		
LIX 84 (%)	TOA (%)	D2EHPA (%)	Cu(II) (ppm)	Cr(VI) (ppm)	Zn(II) (ppm)	Cu(II) (ppm)	Cr(VI) (ppm)	Zn(II) (ppm)
10	5	15	110	153	147	34	10	8.4
15	5	15	110	153	147	5.4	3.5	10.5
15	5	10	110	153	147	5.2	8.0	17.5
15	10	10	110	153	147	32.0	1.12	85.5

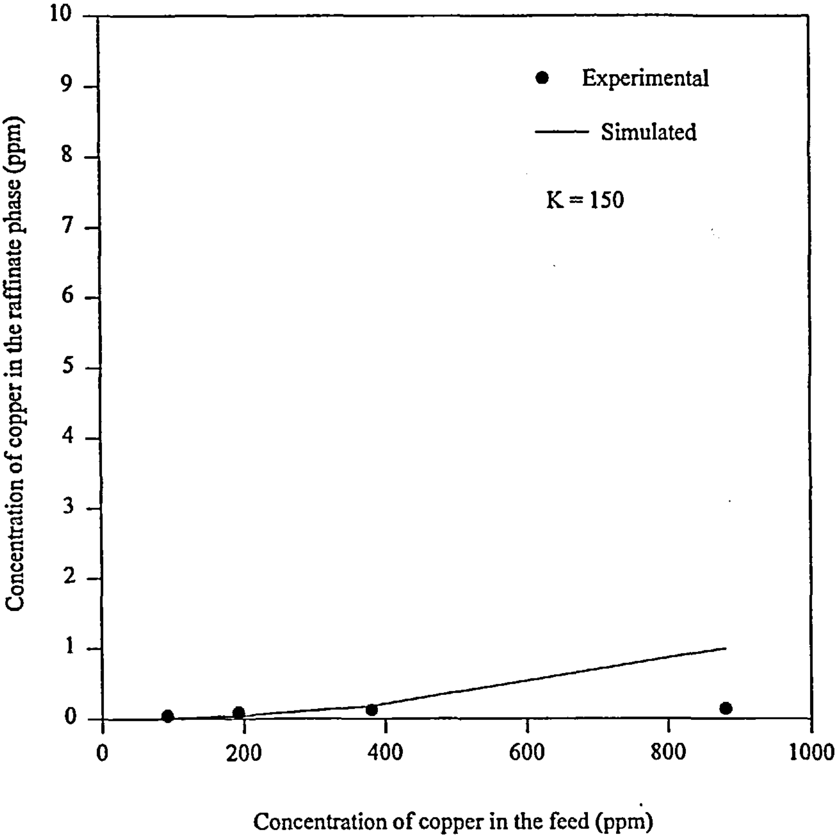

FIG. 7 Comparison between experimental results and simulated results for batch extraction of Cu(II) with a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene.

experimental results when K was 150. Simulated raffinate Cu(II) concentration and pH were closer to the experimental raffinate Cu(II) concentration and pH when a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene was used compared to when a mixed extractant containing 0.234 M LIX 84 + 0.234 M TOA was used. Figures 7 and 8 show comparisons between the experimental results and simulated results for the batch extraction of copper with a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA. The model appears to describe the observed behavior well. Poorer predictions by the model at a higher extractant loading (0.234M LIX 84 + 0.234M TOA) may be due to the neglect of additional reactions and the species formed by such reactions.

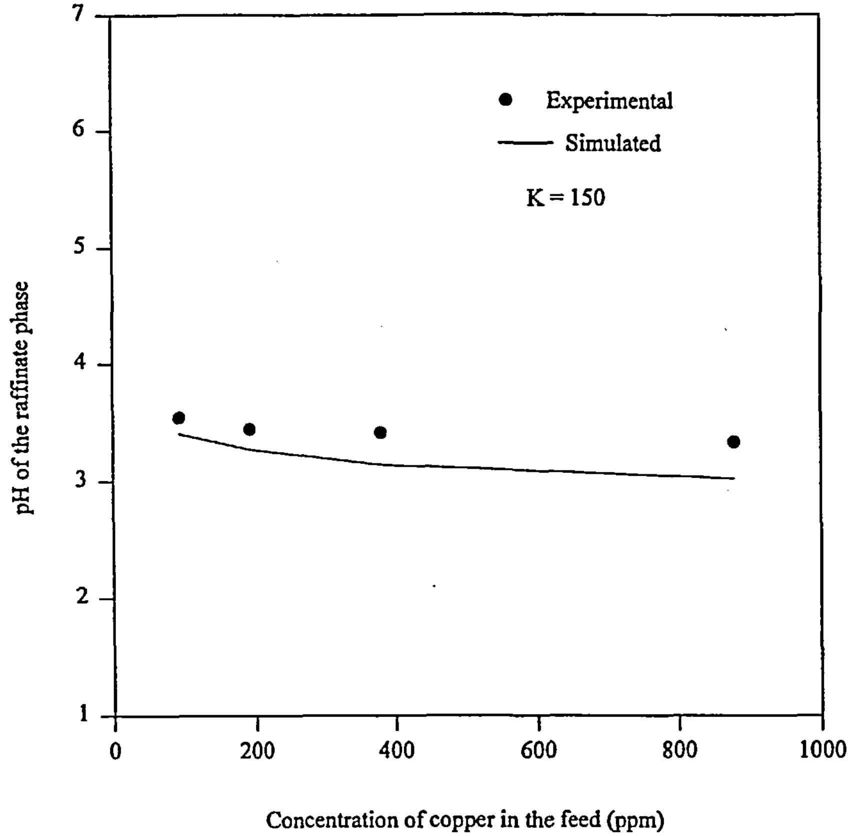

FIG. 8 Comparison between experimental results and simulated results of raffinate pH for batch extraction of Cu(II) with a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene.

CONCLUDING REMARKS

1. Batch experimental results for the copper and chromium system showed that a mixed extractant containing LIX 84 and TOA in kerosene can be efficiently used for the simultaneous removal of copper and chromium. Distribution coefficients of copper and chromium were dependent on the feed concentration of the metal ions and the mixed extractant composition. Raffinate phase pH was also dependent on the feed concentration of the metal ions and the mixed extractant composition.

2. Batch experimental results for the copper, zinc, and chromium system showed that a mixed extractant containing LIX 84, D2EHPA, and TOA in kerosene could be efficiently used for the simultaneous removal of copper, zinc, and chromium. Extraction of copper, zinc, and chromium was highly dependent on the relative concentrations of LIX 84, D2EHPA, and TOA in the mixed extractant. A starting feed pH of 4.0 could be used for efficient extraction performance. A mixed extractant containing D2EHPA and TOA in kerosene could be efficiently used for the simultaneous removal of zinc and chromium.

3. Preliminary modeling of Cu(II) extraction in a batch system of mixed extractants containing LIX 84 and TOA in kerosene has been carried out. Reasonable estimates could be obtained for raffinate Cu(II) concentration and pH when this model was employed. Simulated raffinate Cu(II) concentration and pH were closer to experimental raffinate Cu(II) concentration and pH when a mixed extractant containing 0.156 M LIX 84 + 0.156 M TOA in kerosene was used compared to when a mixed extractant containing 0.234 M LIX 84 + 0.234 M TOA in kerosene was used.

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