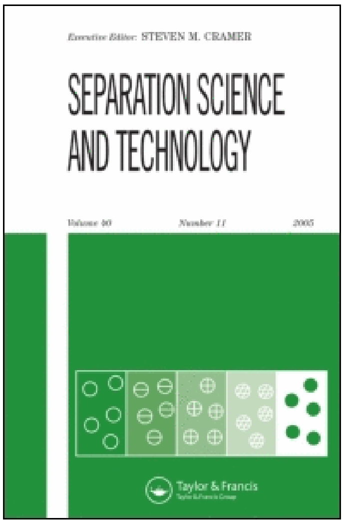

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Liquid–Liquid Extraction of Zinc with High-Molecular-Weight Amines from Alkaline Cyanide Solutions

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Abstract

Quaternary amines are unique in their ability to extract metal cyanides from highly alkaline solutions. Zinc cyanide extracts essentially quantitatively at both the subnanogram and macro levels. Regeneration of the amine solvent is achieved by stripping the zinc with sodium hydroxide, sodium hypochlorite, or alkaline or acidic formaldehyde solutions. Because they readily extract free cyanide as well as anionic metal cyano complexes, the high-molecular-weight quaternary amines show considerable promise for industrial pollution abatement applications.

INTRODUCTION

The need for new and improved waste treatment technology by the metal-finishing industry has recently been reviewed (*1*). Thousands of metal-finishing plants in the United States will require better pollution abatement methods to meet the national priority of reducing discharges. In recent papers (*2–4*) we described studies on the liquid–liquid extraction of mercury and cadmium with high-molecular-weight amines from chloride, iodide, and bromide solutions. In the present study we have extended our investigation to the solvent extraction of metal cyanides. Because of their unique ability to extract metal cyanides from highly alka-

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line solutions, the quaternary amines show considerable potential for pollution abatement applications in the metal-finishing industry.

EXPERIMENTAL

Apparatus

A NaI (Tl) well-type scintillation counter, 1.75 × 2 in., was used for gamma counting.

Reagents

Aliquat 336-S, methyl tri(C_8–C_{10})ammonium chloride is a quaternary amine chloride available from General Mills, Inc., Kankakee, Illinois. Average molecular weight is 442. As supplied by the vendor, the amine is about 90% pure.

Amsco 125–82 is an aliphatic solvent available from Union Oil Co. of California, Amsco Div., Palatine, Illinois 60067.

Tridecyl alcohol is available from Exxon Chemical Co., P.O. Box 3272, Houston, Texas 77001.

Zinc-65 tracer is available from New England Nuclear Co., Boston, Massachusetts.

All other chemicals were reagent grade.

Aliquat 336-S-Cl-Amsco (5% TDA), 0.1 *M*. Dilute 50 g of Aliquat 336-S and 50 ml of tridecyl alcohol to 1 liter with Amsco 125–82. Mix well. To wash out aqueous soluble impurities extract twice for 5 min with equal volume portions of 0.1 *M* NaCl. Centrifuge or filter the organic phase and pour it into a glass reagent bottle.

Aliquat 336-S-CN-Amsco (5% TDA), 0.1 *M*. To convert the amine chloride to the cyanide salt, apply four 5-min extractions with equal volume portions of 2 *M* NaCN. Centrifuge or filter the organic phase and pour it into a glass reagent bottle.

Evaluation Procedure

Ten milliliters of the indicated aqueous phase containing 1×10^5 gamma counts/min/ml of ^{65}Zn tracer was extracted at room temperature with an equal volume portion of the various solvents in 50 ml heavy duty glass centrifuge tubes. Three minute mixing periods were selected arbitrarily. High-speed motor stirrers equipped with glass paddles were used for the extractions. After extraction, the tubes were centrifuged in a clinical centrifuge for 2 min. Each phase was then analyzed for ^{65}Zn by counting 1 ml aliquots in a well-type gamma scintillation counter.

RESULTS AND DISCUSSION

A brief evaluation of selected tertiary, secondary, and primary amines as possible extractants for zinc from alkaline cyanide solution (pH $\geqslant$ 10) was made. As expected, the extractability of zinc cyanide was $<1\%$ in all cases. Therefore, we concentrated on the quaternary amine which is a powerful extractant for metal cyanides from alkaline solution.

The mechanism of extraction of zinc from aqueous cyanide solutions with a quaternary amine is of the type:

$$Zn^{2+} + 4(CN)^- \rightleftarrows Zn(CN)_4{}^{2-}$$

$$[Zn(CN)_4]_a{}^{2-} + 2(R_4NX)_o \rightleftarrows [(R_4N)_2Zn(CN)_4]_o + 2(X)_a{}^-$$

where R_4NX is a selected quaternary amine cyanide or chloride, "a" signifies the aqueous phase, and "o" signifies the organic phase. The quaternary amine and its salt with the anionic cyano or chloro complex of zinc are essentially insoluble in aqueous solutions but highly soluble in most organic solvents.

A wide variety of organic solvents may be used as diluents for the amine. Because of our interest in process application, most of the work to date has used the aliphatic diluents, *N*-dodecane, and Amsco 125–82, and the aromatic diluent, diethylbenzene. The aliphatic diluents require a solvent modifier, 5% tridecyl alcohol (TDA), to increase amine salt solubility and improve the mechanical behavior of the solvent. In the early exploratory extractions we used *n*-dodecane as diluent for the amine. Amsco 125–82 was later selected as diluent because of its more desirable properties for industrial applications. We detected no significant difference in zinc extractability between the two diluents.

The extraction of ^{65}Zn tracer (<1 μg/ml Zn) with Aliquat 336-S–CN–*n*-dodecane as a function of NaCN concentration and alkalinity is shown in Table 1. Zinc-65 tracer extracts very efficiently over a wide range of NaOH concentrations. Depending on the NaCN concentration, the extractability of zinc tracer begins to decrease at about 6 *M* NaOH. This ability of a solvent to extract metal cyanides from very dilute cyanide solution is necessary for treatment of industrial electroplating rinses. Further studies showed that the aromatic diluent, diethylbenzene, was as satisfactory as Amsco for the extraction.

TABLE 1

Extraction of ^{65}Zn Tracer from NaCN Solutions with 0.1 *M* Aliquat 336-S-CN-Dodecane (5% TDA)

Aqueous phase			
NaCN (*M*)	NaOH (*M*)	Equilibrium pH	^{65}Zn extracted (%)
0.0002		9.8	43.5
0.0002		10.3	78.3
0.0002		12.0	> 99.9
0.0002		12.5	> 99.9
0.0002	1–2		99.9
0.0002	4		96.5
0.0002	6		84.8
0.002		9.8	50.0
0.002		10.3	96.7
0.002		12.0	99.8
0.002		12.5	> 99.9
0.002	1–2		99.9
0.002	4		98.6
0.002	6		86.5
0.02		10.3–12.5	> 99.9
0.02	1–2		> 99.9
0.02	4		99.1
0.02	6		93.6
0.02	7.5		65.0

TABLE 2

Extraction of Macroconcentrations of Zinc from 0.4 *M* NaCN Solution with 0.1 *M* Aliquat 336-S-CN-Dodecane (5% TDA)

Zinc concentration (mg/ml)	Zn extracted (%)
< 0.001	> 99.9
0.2	> 99.9
0.6	> 99.9
1	> 99.9
2	99.9
4	78.1
6	52.9
8	40.8

The extraction of macro concentrations of zinc from 0.4 *M* NaCN solution is shown in Table 2. The amine-to-zinc mole ratio is 2. Similar studies in which zinc was extracted as a function of amine concentration also gave an amine-to-zinc mole ratio of 2. Equilibrium is attained rapidly in this system; a 1-min mixing time is sufficient.

Interestingly, free cyanide ion itself is highly extractable in this system. This offers promising potential industrial applications for removing both the metal cyanide complex and the cyanide ion from alkaline solutions.

Several experiments were made using another quaternary ammonium chloride, Adogen 464 (available from Ashland Chemical Co., Columbus, Ohio). The results indicated that Adogen 464 was as efficient as Aliquat-336-S for the metal cyanide extraction.

STRIPPING OF ZINC FROM THE QUATERNARY AMINE SOLVENT

Having extracted zinc and cyanide, the problem is then to recover these materials (strip them from the solvent) so that the solvent can be reused, and the zinc and cyanide can be recycled. The very high stability of the metal cyano complexes in alkaline solution make them most difficult to remove from the solvent. This serious problem of stripping the solvent of cyanide and cyanide metal complexes has been cited by other workers (*5*). They reported that in no case was adequate stripping satisfactorily achieved. Because efficient stripping of the solvent is mandatory for a practical abatement process, we spent considerable effort in this area.

About 30 reagents were investigated as strippants for zinc. Among the few reagents which stripped zinc from the quaternary amine-cyanide solvent were sodium sulfide, potassium iodide, sodium hydroxide, sodium hypochlorite, and formaldehyde. Detailed stripping studies were made using the last three reagents. The organic solvent initially containing 2 mg/ml zinc was stripped by extracting for 3 min with equal volume portions of the various strippants.

Sodium hydroxide is an attractive strippant because it offers the possibility for direct recycle of zinc and cyanide back to electroplating baths. Table 3 shows the stripping of ^{65}Zn tracer from the amine solvent at room temperature with NaOH as a function of amine concentration. The strippability of zinc with NaOH varies inversely with amine concentration. Depending on the amine and NaOH concentrations used, the zinc can be quantitatively stripped from the solvent in two or three stages. Amine solubilities in the NaOH strippant solutions are very low. Typically, 10 *M*

TABLE 3

Stripping of ^{65}Zn Tracer from Aliquat 336-S–CN–Amsco (5% TDA) with Sodium Hydroxide

Aliquat 336-S–CN Concentration (*M*)	Strippant NaOH (*M*)	^{65}Zn tracer stripped (%)
0.01	1	12.9
	3.75	97.7
	7.50	> 99.0
0.05	3	1.6
	8	40.0
	10	82.5
	12	98.5
0.1	7.5	3.2
	10	14.7
	12	37.4
	15	86.0

TABLE 4

Stripping of Zinc[a] from 0.1 *M* Aliquat 336-S–CN–Amsco (5% TDA) with Sodium Hypochlorite

NaOCl strippant, available Cl_2 (%)	Zn stripped (%)
0.4	< 1.0
0.9	2.2
1.7	29.3
2.0	37.0
3.0	66.8
4.0	92.0
4.3	> 99.0

[a]Zinc conc = 2 mg/ml.

NaOH strippants contained <0.5 ppm of the amine solvent. Several further experiments showed that the zinc stripping yields from 0.1 *M* amine solvent could be approximately doubled by using 10 or 12 *M* NaOH at 50°C.

Sodium hypochlorite is also an effective strippant for zinc (Table 4). The hypochlorite destroys the cyanide in the solvent with subsequent precipitation of zinc hydroxide in the aqueous phase. No oxidation losses of the amine were detected even at the highest concentrations of hypochlorite tested. The stripped organic solvent could be reused to extract zinc essentially quantitatively from cyanide solutions. Similar tests with zinc tracer (<1 μg/ml Zn) indicated that it could be quantitatively stripped from the solvent with ⩾2.5% sodium hypochlorite.

Further studies indicated that alkaline or acidic formaldehyde solutions were excellent reagents for stripping zinc from the quaternary amine cyanide solvent (Tables 5 and 6). Formaldehyde complexes the cyanide ion in the solvent, thereby releasing the zinc to the aqueous phase. Zinc hydroxide does not precipitate provided the equilibrium pH is <7 or >11.5.

TABLE 5

Stripping of Zinc[a] from 0.1 *M* Aliquat 336-S–CN–Amsco (5% TDA) with Alkaline Formaldehyde Solutions

Strippant composition		
HCHO (vol-%)	NaOH (*M*)	Zinc stripped (%)
1.2	3.3	20.6
5.8	3.3	57.3
11.5	0.3	53.2
11.5	0.7	75.5
11.5	1.3	98.5
11.5	2.0	99.0
11.5	3.3	99.6
11.5	6.7	73.8

[a]Zinc conc = 2 mg/ml.

TABLE 6

Stripping of Zinc[a] from 0.1 *M* Aliquat 336-S–CN–Amsco (5% TDA) with Acidic Formaldehyde Solutions

Strippant composition			
HCHO (vol-%)	$NH_4C_2H_3O_2$ (*M*)	Equilibrium pH	Zinc stripped (%)
None	1.0	8.0	< 0.1
1.2	0.7	5.2	6.5
5.8	0.7	4.5	75.0
11.5	0.7	4.5	96.4
3.3	0.1	8.0	> 99
3.3	0.2	5.3	95.3
3.3	0.3	5.1	81.2
3.3	0.5	4.6	45.8
3.3	0.7	4.5	37.3

[a]Zinc conc = 2 mg/ml.

TABLE 7

Recovery of Zinc from Alkaline Cyanide Solution with 0.05 *M* Aliquat 336-S–Amsco via Two-Cycle Process

	Zn recovered (%), solvent			
	0.05 *M* Aliquat 336-S–CN–Amsco (5% TDA)		0.05 *M* Aliquat 336-S–Cl–Amsco (5% TDA)	
Process step	^{65}Zn tracer	Zn, 1 mg/ml	^{65}Zn tracer	Zn, 1 mg/ml
Initial extraction	> 99.9	99.9	99.6	95.3
12 *M* NaOH strippant	97.4	94.3	99.8	98.7
Second-cycle extraction	> 99.9	98.5	99.5	96.7
Second-cycle strippant	99.8	96.8	> 99.9	97.6

Yields of zinc were determined in a two-cycle laboratory scale batch process. Two feed solutions were evaluated. One solution contained 0.01 *M* NaCN and 1×10^5 gamma counts/min/ml of ^{65}Zn (<1 μg/ml zinc). The other solution contained 0.01 *M* NaCN and 1 mg/ml of zinc. Twenty-five milliliters of the feed solution was extracted at room temperature for 3 min with 25 ml of 0.05 *M* Aliquat 336-S–CN–Amsco (5% TDA). The zinc was then stripped from the solvent by extracting for 3 min with an equal volume portion of 12 *M* NaOH. The regenerated solvent was then used in a second cycle to extract a fresh portion of the sodium cyanide feed solution. The zinc was then stripped in a manner identical to that used in the first cycle. Similar runs were made with 0.05 *M* Aliquat 336-S–Cl–Amsco (5% TDA) as solvent. The results (Table 7) indicate high recoveries for zinc throughout the two-cycle process with either the cyanide or chloride salt of the amine solvent. A major practical advantage of the amine chloride solvent is that it is considerably easier to regenerate than the amine cyanide solvent. Thus 2 *M* NaOH was as effective as 12 *M* NaOH for stripping zinc from the amine chloride solvent, but it stripped negligible zinc from the amine cyanide solvent.

Applications

High-molecular-weight quaternary amines are excellent extractants for zinc cyanide and cyanide ion from alkaline cyanide solutions. These reagents are especially promising for the isolation, recovery, and pollution abatement applications in the metal-finishing industry. Further chemical studies now in progress will be reported soon on the adaptation of this technique to other cyanide systems (Cd, Ni, Cr) and on the development of continuous, countercurrent solvent extraction processes for pollution abatement applications in this area.

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