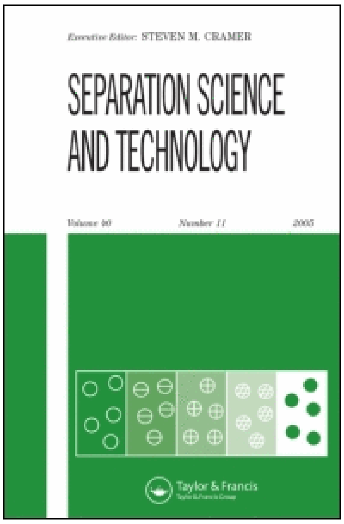

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Solvent Extraction Studies of Zinc with Alamine 336 in Aqueous Chloride and Bromide Media

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Abstract

A study has been undertaken to develop solvent extraction systems for zinc with Alamine 336 in aqueous chloride and bromide media. The parameters studied include acid concentration, halide concentration, pH, reagent concentration, aqueous to organic ratio, and rate of extraction and stripping. The study shows that zinc can be extracted efficiently from both chloride and bromide media. The zinc–Alamine 336 extraction system shows potential for use to remove zinc from polluted industrial wastewater.

INTRODUCTION

Several investigators have reported that zinc can be extracted from aqueous chloride solutions using various high-molecular-weight tertiary amines (HMWTA) (*1–5*). Impure tricaprylamine, a HMWTA which carries the commercial name of Alamine 336, has received considerable research interest in recent years. The sudden flurry of scientific research activity in this particular area can be attributed to the great potential of using Alamine 336 as an extractant to remove various toxic metal ions from aqueous solutions on an industrial scale. Alamine 336 is already being

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produced in huge commercial quantities for other industrial uses. It is therefore readily available at relatively low cost. It is currently being used in the MAR process to remove zinc and other metal ions from certain industrial waste such as lathe turnings and mill shavings (*6*). Alamine 336 has also been recommended to remove zinc from metal finishing wastewater (*7*). The published material to date concerning the zinc–Alamine 336 extraction system falls into two general categories: (1) those investigations which involve the screening of zinc and other metal ions to determine extractability with Alamine 336 and other high molecular weight amine systems and (2) those studies in which zinc or zinc and other metal ions are removed from some industrial aqueous solution using this amine. Although the published investigations are very important, particularly from a practical point of view, they have not included thorough systematic studies of the various parameters which determine the optimum conditions for the extraction of zinc. No such investigations have been reported. This paper will hopefully help fill that important need. Of specific interest is the extraction of trace quantities of zinc ions from aqueous chloride and bromide solutions.

EXPERIMENTAL

Apparatus

A NaI(Tl) well-type scintillation counter, 1.75 × 2.0 inches, consisting of a high voltage power supply, discriminator, and a timer scaler was used for gamma counting. A Perkin-Elmer Model 360 atomic absorption spectrophotometer was used to analyze for zinc in conjuction with the scintillation counter. The accessories include a standard zinc hollow cathode lamp and a Houston Instruments Model 5110–1 Omniscribe Recorder. A Corning Model 119 pH meter with digital display was used for the pH measurements. High-speed motors equipped with glass paddle stirrers were used to mix the phases.

Reagents

Alamine 336 (impure tricaprylamine) is a tertiary amine available from General Mills, Inc., Kanakee, Illinois. A 0.1 *M* stock solution was prepared by dilution with xylene. Solutions of lower concentrations were prepared as needed by further dilution with xylene. Zinc(65) tracer was obtained from Nuclear Sources and Services Inc., Houston, Texas. Zinc standard solutions (1000 ppm) for the atomic absorption spectrophotometer were obtained from the Curtin Scientific Co., Houston, Texas. Deionized water was used throughout the investigation.

Evaluation Procedure

Five milliliters of the indicated aqueous phase containing approximately 1.2×10^4 gamma counts per minute per ml of zinc(65) was extracted at room temperature with an equal volume of 5% (v/v) Alamine 336–xylene in 50 ml heavy-duty centrifuge tubes for 5 min. High-speed motor stirrers equipped with glass paddles were used to carry out the extractions. After extraction, the solutions were centrifuged in a clinical centrifuge for 5 min. Each phase was then analyzed for zinc by counting the gamma activity of 1 ml aliquots of the solution with a well-type gamma scintillation counter. In some cases an atomic absorption spectrophotometer was used to analyze for zinc.

RESULTS

Chloride System

Alamine 336 and its salt with the tetrachlorozincate(II) ion are essentially insoluble in aqueous solutions but show high solubility in xylene.

Several variables associated with the zinc–Alamine 336 aqueous chloride system were studied by use of the evaluation procedure described in the experimental section of this paper. Five percent Alamine 336–xylene was used as the extractant for 20 ppm aqueous zinc unless otherwise specified. Only single batch extractions were investigated.

A study of the effect of Alamine 336 concentration on the extraction efficiency is shown in Table 1. It shows that approximately 95% of the zinc is removed from a 20 ppm zinc solution containing 1.0 *M* HCl using an equal volume of 0.025 *M* Alamine 336–xylene solution. A 0.1 *M* Alamine 336–xylene solution was used in subsequent investigations.

The extraction of zinc using 0.1 *M* Alamine 336 as a function of HCl concentration is shown in Table 2. It shows that an HCl concentration of approximately 0.5 *M* is necessary to remove more than 98% of the zinc. The use of higher HCl concentrations had only a limited effect on the extraction efficiency. A 1.0 *M* HCl solution was chosen for the evaluation procedure.

By keeping the acid concentration (HCl) constant at 0.1 *M* and varying

TABLE 1

Extraction of Zinc as a Function of Alamine 336 Solution[a]

Alamine concentration (M)	Zinc extracted (%)
0.001	7.3
0.0025	27.5
0.005	56.7
0.010	82.6
0.025	94.5
0.05	96.9
0.10	99.25

[a] Initial aqueous solutions contained 20 ppm zinc in 1.0 M HCl.

TABLE 2

Extraction of Zinc as a Function of Hydrochloric Acid Concentration[a]

Hydrochloric acid concentration (M)	Zinc extracted (%)
0.001	2.0
0.024	40.2
0.184	74.6
0.304	92.6
0.484	98.7
0.724	98.6
1.08	99.8

[a] Initial aqueous solutions contained 20 ppm zinc. The organic phase contained 0.1 M Alamine 336–xylene.

the total chloride concentration (HCl + NaCl), a definite dependence on the total chloride concentration was observed. There is a general increase in extraction efficiency with an increase in total chloride concentration. More than 90% removal is achieved in a 0.3 M chloride solution. A 0.7 M solution is required to increase the efficiency to 98%.

The effect of pH is interrelated to the effect of HCl concentration. This study was carried out in a 0.4 M chloride solution. The results show (Table 3) a 99% extraction efficiency if the pH is 1 or less. By raising the pH to 1.7 the extraction efficiency is reduced to 72%. By increasing the chloride concentration as NaCl, there is only a small increase in efficiency at higher pH values.

Equilibrium is reached rapidly; 99% removal of the zinc to the organic phase is achieved in less than 30 sec. Five minute stirring times were chosen for the evaluation procedure, although apparently much shorter stirring periods would have been equally satisfactory.

A study was carried out to determine if large aqueous to organic phase ratios could be efficiently extracted. It showed that aqueous to organic ratios up to 20 to 1 can be extracted at 98% efficiency with 0.1 *M* Alamine 336-xylene solution.

Several aqueous solutions (Table 4) were evaluated to determine their ability to strip zinc from the 5% Alamine-xylene solutions. The organic

TABLE 3

Effect of pH on the Extraction of Zinc with Alamine 336 Solution[a]

Initial pH aqueous phase	Zinc extracted (%)
0.45	100
0.75	99.2
1.02	97.7
1.35	93.6
1.70	72.0
2.18	39.4
13.8	0

[a] Initial aqueous phase contained 20 ppm zinc and 0.4 *M* chloride. The organic phase contained 0.1 *M* Alamine 336-xylene.

TABLE 4

Stripping of Zinc from 5% Alamine 336-Xylene Solutions[a]

Strippant (*M*)		Zinc extracted (%)
NaOH,	0.05	70.7
	0.10	94.7
	0.20	99.9
NH_4OH,	0.1	69.7
	0.2	87.4
	0.5	99.0
	1.0	100.0
EDTA,	0.01	98.6
	0.02	99.7
	0.05	99.3
	0.10	100.0
HNO_3,	0.5	90.6

[a] Organic phase contained 5% Alamine 336 and 20 ppm zinc in chloride media.

phase, initially containing 20 ppm zinc as the tetrachlorozincate(II) complex of Alamine 336, was stripped for 5 min with equal volume aliquots of the various strippants. All the strippants investigated stripped the zinc substantially, with the majority removing more than 90% of the metal from the organic phase with a single stripping operation. The strippants, NaOH $\geq$ 0.2 *M*, $NH_3 \geq$ 0.5 *M*, and EDTA $\geq$ 0.05 *M*, removed more than 99.5% of the zinc.

Bromide System

The data for the bromide system are presented in Tables 5–8. Although in most cases the results observed in the bromide system were quite similar to the chloride system, there were, however, a few cases where the two systems varied significantly. There were some noticeable differences

TABLE 5

Extraction of Zinc as a Function of Alamine 336 Solution[a]

Alamine concentration (*M*)	Zinc extracted (%)
0.0024	21.2
0.005	47.7
0.010	77.6
0.025	94.7
0.05	98.1
0.10	99.2

[a] Initial aqueous solutions contained 20 ppm zinc in 1.0 *M* HBr.

TABLE 6

Extraction of Zinc as a Function of Hydrobromic Acid Concentration[a]

Hydrobromic acid concentration (*M*)	Zinc extracted (%)
0.024	00.0
0.124	7.3
0.200	20.2
0.302	48.1
0.482	72.9
0.722	83.4
1.002	91.5
1.450	98.2
2.180	99.2

[a] Initial aqueous solutions contained 20 ppm zinc. The organic phase contained 0.1 *M* Alamine 336–xylene.

TABLE 7

Effect of pH on the Extraction of Zinc with Alamine 336 Solutions[a]

Initial pH aqueous phase	Zinc extracted (%)
0.23	89.9
0.41	80.5
0.70	60.4
0.85	55.5
1.25	54.8

[a] Initial aqueous phase contained 20 ppm zinc and 0.95 *M* bromide. The organic phase contained 0.1 *M* Alamine 336–xylene.

TABLE 8

Stripping of Zinc from 5% Alamine 336–Xylene Solutions[a]

Strippant (*M*)		Zinc extracted (%)
NaOH,	0.2	99.8
	0.5	99.9
NH_4OH,	0.1	96.0
	0.5	100.0
EDTA,	0.005	99.9
	0.05	100.0
EDA,	0.1	99.5
	0.9	100.0
HNO_3,	0.5	99.8

[a] Organic phase contained 5% Alamine 336 and 20 ppm zinc in bromide media.

in the effect of acid concentration, pH, volume ratio, and stripping studies, as shown in the tables.

DISCUSSION

The mechanism of extraction of zinc from aqueous chloride or bromide solutions with Alamine 336 is of the type:

$$Zn^{2+} + 4X^{-} \rightarrow ZnX_4^{2-}$$

$$2[R_3N]_o + 2H_a^{+} \rightarrow 2[R_3NH]_o^{+}$$

$$2[R_3NH]_o^{+} + ZnX_4^{2-} \rightarrow [R_3NH]_2ZnX_{4o}$$

where R_3N = Alamine 336
o = organic phase
a = aqueous phase

The complex formed by the reaction of tetrahalozincate(II) and Alamine 336 is essentially insoluble in the aqueous phase but shows high solubility in common nonpolar organic solvents. Our studies show that the extraction efficiency is a function of pH. Extractions carried out in highly acidic medium are more efficient than those carried in neutral or alkaline solutions. The acid dependency is shown in the equations explaining the mechanism.

Although the chloride and bromide systems were remarkably similar, there did appear to be some differences that merit discussion. For example, 0.5 *M* HCl solution is needed to extract 98% of the zinc in the chloride system whereas a HBr concentration of greater than 2 *M* is required to remove an equivalent amount of zinc in the bromide system. The same trend was observed in the pH studies; a 99% efficiency was observed at a pH 0.75 in the chloride system whereas at a pH of 0.23 only 90% of the zinc was removed in the bromide system.

It is easier to extract zinc at high aqueous to organic ratios in the chloride system than in the bromide system as shown in the volume ratio studies.

The stripping studies show that it is easier to strip zinc from the organic phase in the bromide system than in the chloride system.

All of these observations give evidence that the tetrachlorozincate(II) anion is more stable than the tetrabromozincate(II) anion.

These conclusions support recent investigations with a zinc–quartenary ammonium salt extraction system (*8*).

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