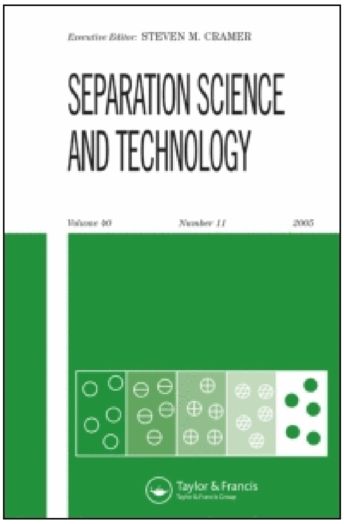


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# Liquid–Liquid Extraction of Cadmium with Alamine 336 from Aqueous Chloride and Bromide Media

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## Abstract

Studies have been made of variables such as reagent concentration, acid concentration, pH, mixing time, settling time, volume ratio, and stripping in order to develop optimum conditions to extract cadmium from aqueous chloride and bromide solutions. A 4-ppm cadmium solution can be extracted essentially quantitatively with an equal volume of 5% Alamine 336-xylene solution in 15 sec. Aqueous to organic ratios up to 20 to 1 can be utilized without loss of extraction efficiency. More than 98% of the extracted cadmium can be stripped from the nonaqueous layer with a series of aqueous strippants including 0.1 *M* EDTA, 1 *M* NaOH, and 2.5 *M* ammonia.

## INTRODUCTION

With the increasing concern for improving the quality of water entering our municipal sewer systems and inner waterways, there has been a great flurry of scientific research activity designed to develop pollution abatement programs for industrially generated wastewater. Cadmium, along with several other toxic metals, is of particular concern. The toxicity of cadmium to humans is well established (*1*). Cadmium generally enters the

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environment through the metal finishing, paint, and zinc smelting industries.

Solvent extraction methods are becoming increasingly important in pollution abatement processes for toxic metals. Several extraction processes have recently been instituted to remove toxic metals from industrial waste. The Gullspang process is used to remove cobalt, nickel, zinc, iron, and chromium from solid industrial waste such as scrap, lathe turnings, and mill shavings (*2*). The MAR process is used to remove zinc, copper, iron, nickel, and chromium from hydroxide slime generated by the metal finishing industry. Both of these industrial processes involve solvent extraction processes using commercially available high molecular weight amines. One of the high molecular weight amines which is available in huge commercial quantities and has received considerable industrial interest in recent years is Alamine 336 (*2*).

The success of Alamine 336 for developing solvent extraction processes for other metals indicates studies should be initiated which would eventually lead to developing processes to remove cadmium from polluted water. Before any industrial process can be developed, basic laboratory-scale studies need to be undertaken. Several investigators have carried out screening studies which indicated cadmium can be extracted from aqueous solutions using Alamine 336 (*3*, *4*). These studies did not investigate thoroughly the various parameters which determine the optimum extraction efficiency. This paper is designed to fulfill that important need.



## EXPERIMENTAL

### Apparatus

A Perkin-Elmer Model 360 Atomic Absorption Spectrophotometric unit with digital display was used to analyze for cadmium. The accessories include a standard cadmium hollow cathode lamp and a Houston Instrument Model 5110–1 Omniscribe Recorder.

A Corning Model 119 pH meter with digital display was used for the pH measurements.

High-speed motors available from Universal Electric Company, Owosse, Michigan, equipped with glass paddle stirrers were used to mix the phases.

An International IEC Clinical Centrifuge with four angles and horizontal head available from Fisher Scientific Company was used to separate the organic phase from the aqueous phase.

Forty milliliter Pyrex brand Model 8260 thick-walled, round-bottom clinical centrifuge tubes were used for the phase separations.

A General Electric Model 19705 spring mechanism interval timer was used to measure the time of mixing and separating the phases.

### Reagents

Alamine 336 (impure tricaprylamine) is a tertiary amine available from General Mills, Inc., Kankakee, Illinois. A 5% (v/v) Alamine 336 stock solution was prepared by dilution with reagent grade xylene for the cadmium investigation. Solutions of lower concentrations were prepared as needed from the stock solution by further dilution with xylene.

Aqueous standard cadmium (1000 ppm) for atomic absorption spectrophotometric analysis was obtained from Curtin-Matheson Company. Solutions of lower concentrations were prepared by dilution with deionized water.

All other chemicals used were of reagent grade. Deionized water was used for all aqueous solution and dilutions. Xylene was used as a solvent and diluent for the organic phase.



### Evaluation Procedure

A typical extraction procedure involved taking 5 ml of 4 ppm cadmium dissolved in 1 *M* hydrochloric acid (in chloride system) or hydrobromic acid (in bromide system) and extracting at room temperature with equal volume portions of 5% Alamine 336 solution in 40 ml heavy duty glass centrifuge tubes for 2 min. High-speed motor stirrers equipped with glass paddles were used to carry out the extractions. After extraction the tubes were centrifuged in a clinical centrifuge for 2 min. Each phase was analyzed for cadmium using an atomic absorption spectrophotometer. If the cadmium concentration was too high (greater than 4 ppm), dilutions with deionized water prior to measurement were necessary.

## RESULTS

### Chloride System

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

The pertinent variables associated with the cadmium–Alamine 336 aqueous chloride extraction system were studied by use of the evaluation procedure previously described. Five percent Alamine 336–xylene and 4 ppm cadmium solutions were used unless otherwise specified. Only single extractions were investigated.

A study of the effect of Alamine 336 concentration indicated that at least a 5% solution was necessary to quantitatively remove the cadmium in an equal aliquot of a solution which is 4.0 ppm in cadmium and 1 *M* in HCl. There was no measureable extraction observed when attempts were made to extract cadmium from aqueous chloride solutions with pure xylene. A 5% Alamine 336–xylene solution was used in subsequent investigations.

The extraction of cadmium using 5% Alamine 336 as a function of HCl concentration is shown in Table 1. It shows that the cadmium must be dissolved in at least 1 *M* HCl in order to extract more than 99% of the metal from 4.0 ppm solution. A cadmium solution containing 1.0 *M* HCl was adopted for the evaluation procedure.

The effect of pH on the extractability of cadmium is shown in Table 2. The pH effect is understandably closely related to that of HCl. The cadmium solutions used in the study contained approximately 1 *M* chloride principally added as NaCl. The table shows that over 97% of the cadmium is extracted up to a pH of 7.

Equilibrium is reached rapidly; more than 98% of the cadmium is transferred from the aqueous to the organic phase by mixing the phases for only 5 sec. Three-minute stirring times were chosen for the evaluation procedure although apparently much shorter stirring periods would have been satisfactory.

A study was carried out to determine the minimum settling time for



TABLE 1

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

| Hydrochloric acid concentration (*M*) | Cadmium extracted (%) |
|---|---|
| 0.05 | 87.16 |
| 0.1 | 95.65 |
| 0.25 | 97.22 |
| 0.5 | 98.52 |
| 1 | 99.10 |
| 2 | 99.08 |

[a] Initial aqueous solutions contained 4 ppm cadmium and 5% Alamine 336.

TABLE 2

Effect of pH on the Extraction of Cadmium with Alamine 336–Xylene[a]

| Initial pH, aqueous phase | Cadmium extracted (%) |
|---|---|
| 1 | 99.28 |
| 2 | 99.37 |
| 3 | 98.73 |
| 4 | 97.07 |
| 5 | 97.12 |
| 6 | 98.10 |
| 7 | 97.56 |
| 8 | 29.46 |
| 9 | 24.26 |
| 10 | 17.65 |

[a] Initial aqueous phase contained 4 ppm cadmium in 1 *M* chloride.



complete phase separation. By allowing the two phases to settle for approximately 5 min, the phase separation is essentially complete, but even after 10 min the interface between the phases is not sharp. The problem was prevented by centrifuging the solution. A 90-sec centrifuge time proved satisfactory for complete phase separation. A slightly longer centrifuge time of 2 min was chosen for the evaluation procedure.

Several aqueous solutions (Table 3) were evaluated to determine their ability to strip cadmium from 5% Alamine 336–xylene solutions. The organic phase initially containing 4 ppm cadmium as the tetrachlorocadmate(II) complex of Alamine 336 was stripped for 5 min with equal volume portions of the various strippants. All the strippants investigated stripped the cadmium substantially with the majority removing more than 90% of the element from the organic phase with a single stripping operation. The strippants, 0.1 *M* EDTA, 1 *M* NaOH, and 5 *M* $HNO_3$, removed more than 99.5% of the cadmium.

A study was carried out to determine if large aqueous to organic phase ratios could be successfully extracted. The data in Table 4 show that more than 99% of the cadmium can be removed up to an aqueous to organic phase ratio of 20 to 1. Close to 90% of the metal is removed at a ratio of 100 to 1.

## Bromide System

The same studies carried out for the chloride system were repeated for the bromide system. Cadmium bromide, hydrobromic acid, and sodium

TABLE 3

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

| Strippant | Cadmium extracted (%) |
|---|---|
| $Na_2S$, 1 *M* | 46.46 |
| $Na_2SO_3$, 1 *M* | 96.87 |
| NaOH, 0.1 *M* | 88.46 |
| 0.25 *M* | 90.22 |
| 0.5 *M* | 98.85 |
| 1 *M* | 99.99 |
| 2 *M* | 99.8 |
| $NH_4OH$, 2.5 *M* | 98.07 |
| $HNO_3$, 5 *M* | 99.75 |
| 1.5 *M* | 76 |
| 1.25 *M* | 6 |
| EDTA, 0.1 *M* | 99.52 |
| 0.05 *M* | 96 |
| 0.02 *M* | 64 |
| KOCN, 5 *M* | 94.38 |
| KSCN, 5 *M* | 91.81 |

[a] Organic phase contained 5% Alamine 336 and 4 ppm cadmium in chloride media.



TABLE 4

Volume Ratio Studies[a]

| Volume ratio, aqueous:organic | Cadmium extracted (%) |
|---|---|
| 1:1 | 99.91 |
| 2:1 | 99.89 |
| 5:1 | 99.73 |
| 10:1 | 99.28 |
| 20:1 | 98.08 |
| 50:1 | 88.3 |
| 100:1 | 89.71 |

[a] Initial cadmium concentration was 4 ppm in 1 *M* hydrochloric acid.

TABLE 5

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

| Hydrobromic acid concentration (*M*) | Cadmium extracted (%) |
|---|---|
| 0.05 | 98.85 |
| 0.1 | 95.21 |
| 0.25 | 97.08 |
| 0.5 | 98.40 |
| 1 | 99.66 |
| 2 | 99.50 |

[a] Initial aqueous solutions contained 4 ppm cadmium and 5% Alamine 336.

TABLE 6

Effect of pH on the Exytaction of Cadmium with Alamine 336–Xylene[a]

| Initial pH, aqueous phase | Cadmium extracted (%) |
|---|---|
| 1 | 99.61 |
| 2 | 99.49 |
| 3 | 99.38 |
| 4 | 99.45 |
| 5 | 97.93 |
| 6 | 97.55 |
| 7 | 95.52 |
| 8 | 28.96 |
| 9 | 23.96 |
| 10 | 23.72 |

[a] Initial aqueous phase contained 4 ppm cadmium in 1 *M* bromide.



bromide were substituted for their corresponding chloride compounds. The data for the bromide system are shown in Tables 5, 6, 7, and 8. They show that there are only minor differences in the two systems.

## DISCUSSION

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

$$Cd^{2+} + 4X^- \rightleftarrows CdX_4^{2-}$$

$$2[R_3N]_o + [CdX_4^{2-}]_{aq} + [2H_{aq}^+] \rightleftarrows [(R_3NH)_2CdX_4]_o$$

where $R_3N$ = Alamine 336, o = organic phase, and aq = aqueous phase.

TABLE 7

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

| Strippant | Cadmium stripped (%) |
|---|---|
| $Na_2S$, 1 *M* | 44.60 |
| $Na_2SO_3$, 1 *M* | 90.60 |
| NaOH, 0.1 *M* | 84.20 |
| 0.25 *M* | 87.12 |
| 0.5 *M* | 95.63 |
| 1 *M* | 98.60 |
| 2 *M* | 97.80 |
| $NH_4OH$, 2.5 *M* | 98.25 |
| $HNO_3$, 5 *M* | 98.95 |
| 1.5 *M* | 60 |
| 1.25 *M* | 8 |
| EDTA, 0.1 *M* | 99.60 |
| 0.05 *M* | 97.60 |
| 0.02 *M* | 97.20 |
| KOCN, 5 *M* | 75.87 |
| KSCN, 5 *M* | 61.89 |

[a] Organic phase contained 5% Alamine 336 and 4 ppm cadmium in bromide media.



TABLE 8

Volume Ratio Studies[a]

| Volume ratio, aqueous: organic | Cadmium extracted (%) |
|---|---|
| 1:1 | 99.97 |
| 2:1 | 99.62 |
| 5:1 | 99.03 |
| 10:1 | 99.00 |
| 20:1 | 97.38 |
| 50:1 | 85.43 |
| 100:1 | 83.93 |

[a] Initial cadmium concentration was 4 ppm in 1 *M* hydrobromic acid,

From the equations it can be seen that the tetrahalocadmate(II) ion forms an ion associated complex with Alamine 336 in acid media. The extractability of the ion-associated ion complex can be attributed to the hydrophobic character of the large R groups (capryl) in Alamine 336.

These investigations show that cadmium can be extracted from aqueous chloride or bromide media using 5% Alamine 336. The 4-ppm cadmium concentration used is within the range of that found in much of the wastewater generated by the metal finishing industry, the chief cadmium polluter. The rapid equilibration, fast settling time, and high aqueous to organic phase ratios are essential for industrial applications. Since there is very little difference between the bromide and chloride systems, the chloride would be preferred for economic reasons. The close similarity of the bromide and chloride systems differs from that observed in similar studies of the cadmium–Aliquat 336-S extraction systems (*5–7*). Aliquat 336 is a high molecular weight quaternary ammonium salt.

Alamine 336 is currently being used industrially to extract various metals from industrial wastewater. This investigation indicates that serious consideration should be given to including cadmium in further industrial applications of this versatile extractant.

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