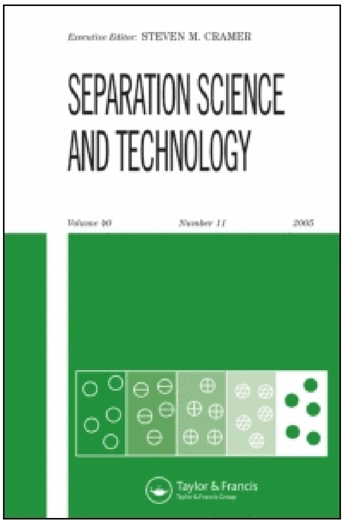

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Zinc Ions from Aqueous Chloride Solutions by Solvent Extraction Using Alamine 308

Curtis W. McDonald[a]; Brenda P. Earhart[a]
[a] DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY, HOUSTON, TEXAS

To cite this Article McDonald, Curtis W. and Earhart, Brenda P.(1979) 'Removal of Zinc Ions from Aqueous Chloride Solutions by Solvent Extraction Using Alamine 308', Separation Science and Technology, 14: 8, 741 — 747
To link to this Article: DOI: 10.1080/01496397908060234
URL: http://dx.doi.org/10.1080/01496397908060234

SEPARATION SCIENCE AND TECHNOLOGY, 14(8), pp. 741–747, 1979

NOTE

Removal of Zinc Ions from Aqueous Chloride Solutions by Solvent Extraction Using Alamine 308

CURTIS W. McDONALD* and BRENDA P. EARHART†

DEPARTMENT OF CHEMISTRY
TEXAS SOUTHERN UNIVERSITY
HOUSTON, TEXAS 77004

Abstract

A study has been undertaken to develop a solvent extraction system for zinc with Alamine 308 in aqueous chloride medium. The parameters investigated included reagent concentration, acid concentration, pH, aqueous to organic phase ratio, and rate of extraction and stripping. The study shows that zinc can be extracted rapidly and efficiently from aqueous chloride solutions. A number of aqueous stripping reagents removed more than 90% of the zinc from the organic phase with only one equilibration.

INTRODUCTION

A number of investigators have reported that trace quantities of 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 been extensively studied in recent years (*6–8*). As a result of this research activity, Alamine 336, which is commercially available in huge quantities at low cost for other industrial uses, is currently being used to extract zinc and other toxic metals from industrial wastewater. Specifically, it is currently being used in the MAR process to remove zinc and other metal ions from

*To whom all correspondence should be addressed.

†Taken partly from a thesis presented to the Graduate School for the Master of Science degree in Chemistry.

industrial wastewater generated from lathe turnings and mill shavings (*9*). Alamine 336 has also been recommended for the removal of zinc from metal finishing wastewater (*10*).

In recent years a number of other HMWTA have become available in commercial quantities at relatively low cost. Due to the success of Alamine 336, there is a need to investigate other HMWTA with similar chemical structures to ascertain the feasibility of their utilization as extractants for zinc and other heavy metals. One such HMWTA is Alamine 308. Alamine 308 is impure triisooctylamine and is also available in commercial quantities at about the same cost as Alamine 336.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 360 atomic absorption spectrophotometer was used to analyze the solutions for zinc. The accessories included a standard zinc hollow cathode lamp and a Houston Instruments Model 5110 recorder. The absorbance measurements were made at 213.9 nm. 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 308 is impure triisooctylamine, a HMWTA commercially available from General Mills, Kanakee, Illinois. A 5% stock solution was prepared by dilution with xylene. Solutions of lower concentrations were prepared as needed from the stock solution by further dilution with xylene.

Standard zinc solution (1000 ppm) was obtained from the J. T. Baker Chemical Co., Phillipburg, New Jersey. Zinc solutions of lower concentrations were prepared from the standard by dilution with deionized water. Deionized water was used to prepare all the aqueous solutions used in the investigation.

Evaluation Procedure

Ten milliliter aliquots of 2.0 ppm zinc solutions containing 0.5 *M* HCl were extracted at room temperature with equal volumes of 5% Alamine

308 in 40 ml centrifuge tubes for 5 min. High-speed moter stirrers equipped with glass paddles were used to carry out the extractions. After equilibration, the solutions were centrifuged in a clinical centrifuge for 5 min. The aqueous phase was then analyzed for zinc at 213.9 nm using an atomic absorption spectrophotometer.

RESULTS

The pertinent variables which determine the optimum conditions to efficiently extract zinc from aqueous chloride solutions using Alamine 308 were studied by use of the evaluation procedure previously described. Two ppm aqueous zinc and 5% Alamine 308–xylene solutions were used unless otherwise specified. Duplicate single batch extractions were used in all investigations.

A study of the effect of Alamine 308 concentration on the extraction efficiency is shown in Table 1. It shows that 83% of the zinc is extracted using a 1% Alamine 308 solution. More than 98% is removed using a 5% solution. Higher concentrations of the HMWTA did not improve the extraction efficiency. A 5% Alamine 308–xylene solution was used in subsequent investigations.

The extraction of zinc using Alamine 308 as a function of HCl concentration is shown in Table 2. It shows that the extraction efficiency increases with HCl concentration up to 0.5 *M*. Higher HCl concentrations did not improve the extraction efficiency. Zinc solutions containing 0.5 *M* HCl were chosen for the evaluation procedure.

The extractability of zinc as a function of pH is shown in Table 3. It shows that the effect of pH is interrelated to the effect of HCl concentra-

TABLE 1

Extraction of Zinc as a Function of Alamine 308 Solution[a]

Concentration of Alamine (%)	Zinc extracted (%)
0.5	66.8
1	83.0
2	93.0
3	93.2
4	95.5
5	98.5
10	98.5

[a]Initial aqueous solutions contained 1 ppm zinc in 0.5 *M* HCl.

TABLE 2

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

Hydrochloric acid concentration	Zinc extracted (%)
0.25	82.0
0.30	82.8
0.40	86.3
0.50	97.0
1.0	94.5
2.0	97.0

[a]Initial aqueous solutions contained 2 ppm zinc. The organic phase contained 5% Alamine 308–xylene.

TABLE 3

Effect of pH on the Extraction of Zinc with Alamine 308 Solution[a]

Initial pH, aqueous phase	Zinc extracted (%)
0.54	98.6
1.06	99.0
2.10	87.0
3.94	35.0
5.12	37.7
5.99	34.9

[a]Initial aqueous phase contained 2 ppm zinc and 2.5 *M* chloride. The organic phase contained 5% Alamine 308–xylene.

tion. To minimize the effect of chloride concentration, the pH study was carried out in 2.5 *M* sodium chloride solutions. The pH of the solution was adjusted using NaOH and HCl. Table 3 shows that the highest extraction efficiency is achieved at a pH of about 1. There is a steady decrease in extraction efficiency as the pH increases. The pH studies in the alkaline range gave inconsistent and erratic results. A possible explanation of these results is the formation of hydrous oxides of zinc in alkaline solutions.

Equilibrium is reached rapidly; over 97% removal of the zinc from the aqueous phase to the organic phase is achieved after stirring for only 5 sec. Five-minute stirring times were chosen for the evaluation procedure, although apparently much shorter stirring periods would have been equally satisfactory. The results of the effect of stirring time are shown in Table 4.

TABLE 4

Effect of Stirring Time on the Extraction of Zinc with Alamine 308 Solution[a]

Stirring time (sec)	Zinc extracted (%)
300	99.0
240	98.5
180	99.0
120	99.7
60	99.6
30	99.9
10	97.5
5	97.5

[a]Initial aqueous phase contained 2 ppm zinc and 0.5 *M* HCl. The organic phase contained 5% Alamine 308–xylene.

A study was carried out to determine if large aqueous to organic phase ratios could be efficiently extracted. It showed a decrease in extraction efficiency with an increase in the aqueous to organic phase ratio. At a 2 to 1 ratio, 98% of the zinc is removed; at a 5 to 1 ratio the efficiency is reduced to 91%, and at a ratio of 20 to 1 the efficiency is 80%.

A number of aqueous solutions were evaluated to determine their ability to strip zinc from 5% Alamine 308–xylene solutions. The organic phase, initially containing 2 ppm zinc as the tetrachlorozincate(II) complex of Alamine 308, was stripped for 5 min with equal volume aliquots of the various aqueous strippants. All the strippants investigated removed more than half of the zinc from the organic phase. Ethylenediamine and EDTA solutions proved to be the most efficient. The results are shown in Table 5.

DISCUSSION

The mechanism of extraction of zinc from aqueous chloride solutions with Alamine 308 is of the type

$$Zn^{2+} + 4Cl^{-} \rightleftarrows ZnCl_4^{2-}$$

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

$$2[R_3NH]_o^{+} + ZnCl_4^{2-} \rightleftarrows [(R_3NH)_2ZnCl_4]_o$$

where R_3N = Alamine 308
o = organic phase
a = aqueous phase

TABLE 5

Stripping of Zinc from 5% Alamine 308–Xylene Solution[a]

Strippant concentration	Zinc extracted (%)
NaOH: 0.05 *M*	75.7
0.5	84.1
NH_4OH: 0.02 *M*	56.1
0.1	58.0
1.0	74.3
Na_2SO_3: 0.1 *M*	66.13
1.0	85.25
EDTA: 0.01 *M*	91.6
0.02	81.0
0.2	97.4
EDA: 0.1%	69.75
0.2%	70.94
0.5%	91.85
1.0%	89.44

[a]Organic phase contained 5% Alamine and 2 ppm zinc in chloride media.

The complex formed by the reaction of the tetrachlorozincate(II) anion and Alamine 308 is essentially insoluble in the aqueous phase but shows high solubility in common nonpolar organic solvents such as xylene. Our studies showed that extractions carried out in acid media are more efficient than those in neutral or alkaline solutions. The acid dependency is shown in the equations describing the mechanism of the reaction.

In general, the zinc–Alamine 308 extraction system compares favorabably with the zinc–Alamine 336 system (*6*). Since both HMWTA are about equivalent in cost and availability, the utilization of Alamine 308 as an industrial extractant for toxic metals in wastewater should be explored.

Acknowledgment

The authors wish to thank the Robert A. Welch Foundation for its generous financial support of this research through grant No. J-653.

REFERENCES

1. M. Mizza et al., *Anal. Chem. Acta*, *37*, 402 (1967).
2. F. Seeley and D. Crouse, *J. Chem. Eng. Data*, *11*, 424 (1966).
3. T. Suzuki and T. Sotobovashi, *J. Chem. Soc. Jpn.*, *87*, 857 (1966).
4. H. Mahlam et al., *Anal. Chem.*, *26*, 1939 (1968).

5. V. S. Schmidt et al., *Radiokhimiya, 9*, 700 (1967).
6. C. McDonald and N. Butt, *Sep. Sci. Technol., 13*, 39 (1978).
7. C. McDonald and G. H. Pahlavan, *Sep. Sci., 12*, 271 (1977).
8. C. McDonald, M. Mahayni, and M. Kanjo, *Sep. Sci. Technol., 13*, 429 (1978).
9. H. Reinhardt, *Chem. Ind.* (March 1, 1975).
10. C. McDonald and R. Bajwa, *Sep. Sci., 12*, 435 (1977).

Received by editor January 16, 1979