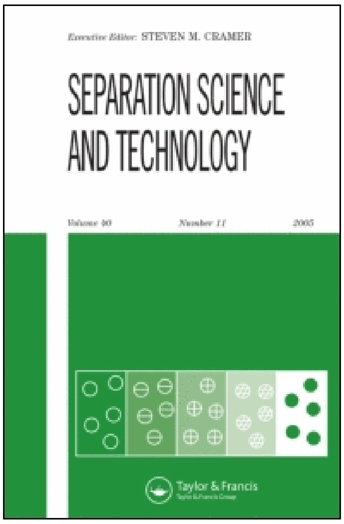

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Solvent Extraction Studies of Lead Using Alamine 336 and Aliquat 336-S

Curtis McDonald[a]; Mohamed M. Mahayni[a]; Marwan Kanjo[a]
[a] DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY, HOUSTON, TEXAS

To cite this Article McDonald, Curtis , Mahayni, Mohamed M. and Kanjo, Marwan(1978) 'Solvent Extraction Studies of Lead Using Alamine 336 and Aliquat 336-S', Separation Science and Technology, 13: 5, 429 — 437
To link to this Article: DOI: 10.1080/01496397808058292
URL: http://dx.doi.org/10.1080/01496397808058292

SEPARATION SCIENCE AND TECHNOLOGY, 13(5), pp. 429–437, 1978

Solvent Extraction Studies of Lead Using Alamine 336 and Aliquat 336-S

CURTIS McDONALD,* MOHAMED M. MAHAYNI,†
and MARWAN KANJO†

DEPARTMENT OF CHEMISTRY
TEXAS SOUTHERN UNIVERSITY
HOUSTON, TEXAS 77004

Abstract

New solvent extraction systems have been developed for the removal of lead ions from aqueous chloride solutions using the high-molecular-weight amines, Alamine 336 and Aliquat 336-S. The lead ions can be extracted with better than 80% efficiency using equal volumes of either 5% Alamine 336 or 5% Aliquat 336-S. The extractions are simple and rapid. The extracted lead can be stripped in both cases using EDTA.

INTRODUCTION

High-molecular-weight amines (HMWA) have been firmly established as excellent extractants for complex anions of various metals (*1–3*). Lead does not form stable anionic complexes in aqueous solutions as readily as many of the transition metals. It does, however, form halide complexes which can be extracted with HMWA. Several investigations have reported that lead can be extracted from aqueous chloride solutions using various HMWA (*4–9*). Generally these investigations represented screening studies in which lead along with other metals was investigated. Moreover, systematic investigations of the parameters which determine

---

*To whom correspondence should be addressed.

†Taken partly from theses submitted to the Graduate School for the MS in Chemistry.

the optimum conditions for extraction of lead using HMWA have not been undertaken.

Alamine 336 and Aliquat 336-S have been extensively used as extractants for mercury (*10*, *11*), cadmium (*12–14*), zinc (*15–17*), and other metals (*18–20*). No such detailed studies using these HMWA have been reported for lead. Lead is highly toxic and its lons in certain industrial wastewater pose a serious pollution abatement problem. Due to the increasing potential of utilizing Alamine 336 and Aliquat 336-S as extractants to remove other toxic metal ions from industrial wastewater, the feasibility of using these versatile extractants for lead needs to be explored. This paper is designed to at least partially meet this important need.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 360 atomic absorption spectrophotometer was used to analyze the solutions for lead. The accessories included a standard lead hollow cathode lamp and a Houston instruments Model 5110 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.

Reaqents

Alamine 336 is impure tricaprylamine, a high-molecular-weight tertiary amine commercially available from General Mills. A 25% stock solution was prepared using xylene as a solvent. Solutions of lower concentrations were prepared by further dilution with xylene.

A 1000 ppm lead standard solution was obtained from the J. T. Baker Chemical Company. Solutions of lower concentrations were prepared by dilution with deionized water.

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

Evaluation Procedure

A typical extraction procedure involved taking 10 ml of 10 ppm lead dissolved in 2 *M* hydrochloric acid and extracting at ambient temperature with equal volume aliquots of 5% Alamine 336 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. The solutions were allowed to settle for 20 min in order for the phases to separate. The aqueous layer was then analyzed for lead using an atomic absorption spectrophotometer. If the lead concentration is too high, dilution with deionized water prior to measurement is necessary.

Results

The pertinent variables of the lead–Alamine 336 system were studied by use of the evaluation procedure previously described. Each solution studied contained 10 ppm lead unless otherwise specified.

A study of the rate of the extraction of lead as a function of Alamine 336 concentration is shown in Table 1. It shows a general increase in extraction efficiency with an increase in extractant concentration. Although only 84% of the lead was removed using 5% Alamine 336–xylene, it was chosen for the evaluation procedure. Very high Alamine 336 concentrations were more efficient in removing the lead, but the concentrated solutions were viscous and somewhat tedious to work with during the extraction process.

A study of the extraction of lead as a function of hydrochloric acid concentration showed an optimum acid concentration of 2 *M*. The data shown in Table 2 indicate a decrease in extraction efficiency at hydrochloric acid concentrations greater than 2 *M*.

TABLE 1

Extraction of Lead as a Function of Alamine 336–Xylene Concentration[a]

Concentration of Alamine 336–xylene	Lead extracted (*E*%)
0.5	31.19
1	53.50
2	64.45
3	70.00
5	84.00
10	92.40
15	95.26
20	98.66
25	99.33
40	100.00

[a] Initial aqueous solutions contained 10 ppm of Pb and 2 *M* hydrochloric acid.

TABLE 2

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

Hydrochloric acid concentration (M)	Lead extracted ($E\%$)
0.1	45.50
0.25	64.50
0.50	75.40
0.75	78.50
1.0	79.40
1.5	83.50
2.0	84.20
2.5	79.61
3.0	74.25
4.0	64.58

[a] Initial aqueous solutions contained 10 ppm of Pb. Extractant: 5% Alamine 336-xylene.

Equilibrium is reached rapidly; less than 1 min of stirring was necessary for maximum removal of the lead. A 2-min mixing period was chosen for the evaluation procedure.

A study was carried out to determine if large aqueous to organic ratios could be efficiently extracted. It showed a steady decrease in extraction efficiency with an increase in aqueous phase to organic phase ratio. Some 84% of the lead is removed using a 1 to 1 ratio. By increasing the ratio to 20 to 1, only 34% of the lead is removed.

Several aqueous solutions were evaluated to determine their ability to strip lead from the Alamine 336-xylene solutions. The organic phase initially containing 10 ppm lead as the chloro lead complex of Alamine 336 was stripped for 5 min with equal volume aliquots of the various strippants. The results shown in Table 3 indicates that of the strippants studied, only EDTA stripped the lead with greater than 99% efficiency.

ALIQUAT 336-S SYSTEM

The studies described herein for the lead–Alamine 336 extraction system were generally carried out in the same manner for the lead–Aliquat 336-S system. The data are shown in Tables 4, 5, and 6. In some cases the results observed for both systems were quite similar. However, there were also significant differences, as shown in the tables.

TABLE 3

Lead Stripping Studies

Strippant	Stripping efficiency (%)
EDTA	
0.001 *M*	98.49
0.0025 *M*	98.99
0.005 *M*	99.10
0.01 *M*	99.10
0.05 *M*	99.70
0.1 *M*	100.00
Na_2SO_3	
0.1 *M*	6.27
0.25 *M*	11.29
0.5 *M*	22.58
1.0 *M*	52.69
NH_4OH	
0.1 *M*	1.15
0.25 *M*	1.90
0.5 *M*	3.20
1.0 *M*	8.78
2.0 *M*	31.99
NaOH	
0.01 *M*	70.12
0.05 *M*	79.87
0.1 *M*	85.53

[a] Organic phase contained 5% Alamine 336–xylene and 10 ppm of Pb in chloride media.

TABLE 4

Extraction of Lead as a Function of Aliquat 336-S-Cl–Xylene Concentration[a]

Concentration of Aliquat 336-S-Cl–xylene (%)	Lead extracted (*E*%)
0.5	56.5
1	63.6
2	71
3	77
4	80.2
5	82.4
6	84.4
8	87.7
10	88.7
15	91.1
20	93.1
25	94.3

[a] Initial pH = 3.33. In 1 *M* chloride ions.

TABLE 5

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

Hydrochloric acid concentration (*M*)	Lead extraction (*E*%)
0.1	67.0
0.2	70.1
0.4	79.9
0.6	82.6
0.8	84.2
1.0	84.8
1.2	84.0
1.4	83.8
1.6	83.1
1.8	82.0
2.0	81.1
2.5	77.1
3.0	73.1

[a] Initial pH = 3.33. Initial aqueous solution contained 100 ppm of Pb. 5% Aliquat 336-S-Cl.

DISCUSSION

The mechanism of extraction of lead from aqueous chloride solution with Alamine 336 is

$$(\mathrm{Pb})_a^{2+} + 3(\mathrm{Cl})_a^- \rightleftarrows (\mathrm{PbCl_3})_a^-$$

$$(\mathrm{PbCl_3})_a^- + \mathrm{H}_a^+ + (\mathrm{R_3N})_o \rightleftarrows \{(\mathrm{R_3NH})(\mathrm{PbCl_3})\}_o$$

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

The mechanism for extracting lead using Aliquat 336-S is

$$(\mathrm{Pb})_a^{2+} + 3(\mathrm{Cl}^-)_a^- \rightleftarrows (\mathrm{PbCl_3})_a^-$$

$$(\mathrm{R_4NCl})_o + (\mathrm{PbCl_3})_a^- \rightleftarrows \{(\mathrm{R_4N})(\mathrm{PbCl_3})\}_o + \mathrm{Cl}^-$$

where R_4NCl = Aliquat 336-S

The complexes formed by the reaction of $PbCl_3^-$ with Alamine 336 and Aliquat 336-S are essentially insoluble in the aqueous phase, but show high solubilities in common nonpolar organic solvents.

Tables 2 and 5 show that there is an initial increase in extraction

TABLE 6

Lead Stripping Studies

Strippant	Stripping efficience (%)
EDTA	
0.05 *M*	84.4
0.1 *M*	75.4
EDA	
5 *M*	59.8
HNO_3	
0.5 *M*	92.5
1.0 *M*	97.2
2.5 *M*	100.0
KOCN	
5 *M*	95.4
KSCN	
5 *M*	83.3
Na_2S	
0.1 *M*	0.0
Na_2SO_3	
1.0 *M*	51.2
NH_4OH	
2.0 *M*	7.0
NaOH	
0.1 *M*	88.7
0.25 *M*	99.3
0.5 *M*	99.9
1.0 *M*	100.0

[a] Organic phase contained 5% Aliquat 336-S-Cl, 81 ppm Pb.

efficiency with an increase in hydrochloric acid concentration followed by a decrease in efficiency for Alamine 336 and Aliquat 336-S systems. An optimum hydrochloric acid concentration of 1 *M* was chosen for the Aliquat 336-S system whereas a 2-*M* solution was chosen for Alamine 336. The mechanism equations show a hydrogen ion dependency in the Alamine 336 system. There is no such dependency in the Aliquat 336-S system. This may explain the higher optimum hydrochloric acid concentration for the Alamine 336 system.

The increase in extraction efficiency with hydrochloric acid can be attributed to the predominance of $PbCl_3^-$ in higher acid concentrations. Presumably the nonextractable species $PbCl^+$ and $PbCl_2$ exist only in extremely low concentrations in hydrochloric acid solutions.

The reason for the decrease in extraction efficiency at very high hydrochloric acid concentrations remains somewhat uncertain. At the high acid concentrations there should be more lead in the form of $PbCl_4^{2-}$ and perhaps $PbCl_6^{4-}$. Since the HMWA are very large bulky molecules, they could be somewhat sterically hindered from forming neutral extractable species with chloro lead complex anions containing multiple negative charges. The same negative dependency at high hydrochloric acid concentrations was observed by Singh and Tandon with several cadmium–HMWA systems (*21*). They attributed it to the formation of HCl_2^- which competed with $PbCl_3^-$ in solution for the HMWA. The existence of the HCl_2^- species was not confirmed experimentally.

The efficiency of the removal of lead decreases as the aqueous to organic ratio increases for the Aliquat 336-S system as is observed for Alamine 336. The same trend was observed if 25% Aliquat 336-S was used instead of 5%. The inability to extract lead efficiently from aqueous solutions using high aqueous to organic ratios using either of the HMWA and the necessity of having relatively high hydrochloric acid concentrations mean that they have limited potential for application to the industrially polluted lead wastewater problem.

Acknowledgments

The authors wish to thank the Division of Basic Energy Sciences of the Development of Energy through Contract No-E-(40-1)-4535 for its generous financial support of the investigation.

REFERENCES

1. V. S. Shmidt, *Amine Extractions*, Keter Press, Jerusalem, 1971, p. 98.
2. F. L. Moore, NAS-NS-3101 (1960).
3. W. J. Maeck et al., *Anal. Chem.*, *33*, 1775 (1971).
4. T. Suzuki and T. Sotoboyashi, *J. Chem., Soc. Jpn., Pure Chem. Soc.*, *87*, 587 (1966).
5. T. Suzuki and T. Sotoboyashi, *Jpn. Anal.*, *14*, 414 (1965).
6. J. C. Sheppard and R. Warnock, *J. Inorg. Nucl. Chem.*, *26*, 1421 (1964).
7. M. Mizza et al., *Anal. Chim. Acta*, *37*, 402 (1967).
8. H. Irwing and A. Nabilsi, *Ibid.*, *41*, 505 (1968).
9. V. F. Borbat et al., *Tsvetn. Met.*, *9*, 37 (1966).
10. F. L. Moore, *Environ. Sci. Technol.*, *6*, 525 (1972).
11. F. L. Moore, *Sep. Sci.*, *7*, 505 (1972).
12. C. W. McDonald and F. L. Moore, *Anal. Chem.*, *45*, 983 (1973).
13. C. W. McDonald and T. S. Lin, *Sep. Sci.*, *10*, 449 (1975).
14. C. W. McDonald and G. H. Pahlavan, *Sep. Sci.*, *12*, 271 (1977).
15. F. Seeley and D. Crouse, *J. Chem. Eng. Data*, *11*, 424 (1966).

16. C. W. McDonald and T. Rhodes, *Sep. Sci.*, *9*, 441 (1974).
17. C. W. McDonald and T. Rhodes, *Anal. Chem.*, *46*, 300 (1974).
18. C. Kopp and R. McDonald, *Solvent Extraction Chemistry*, North-Holland, Amsterdam, 1967, p. 447.
19. F. L. Moore, *Anal. Chem.*, *36*(2), 158 (1964).
20. C. W. McDonald and R. Bajwa, *Sep. Sci.*, *12*, 435 (1977).
21. O. V. Singh and S. N. Tandon, *J. Inorg. Nucl. Chem.*, *36*, 439 (1974).

Received by editor July 30, 1977