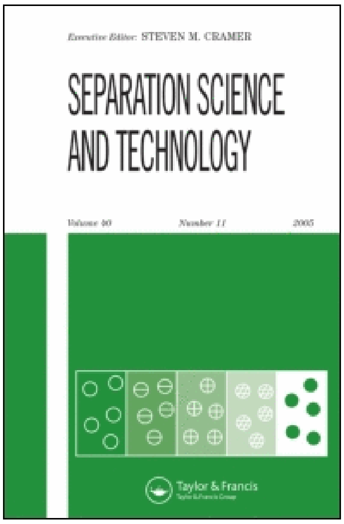

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Liquid-Liquid Extraction of Zinc with Aliquat 336-S-Br from Aqueous Bromide Solutions

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NOTE

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Abstract

A new solvent extraction system has been developed for zinc in aqueous bromide solution using Aliquat 336-S-Br-xylene solution as an extractant. A 1 mg/ml zinc solution is extracted essentially quantitatively with an equal volume of 5% Aliquat 336-S-Br-xylene solution in 15 sec. The extracted zinc can be stripped from the nonaqueous layer with a series of aqueous solutions including Na_2SO_3 ($\geq$ 1.0 *M*), NaOH ($\geq$ 0.5 *M*), NH_3 ($\geq$ 0.5 *M*), ethylenediamine ($\geq$ 0.3%), and EDTA ($\geq$ 0.5%). The extraction is quantitative only from acidic solutions. High aqueous to organic phase ratios can be utilized without loss of extraction efficiency.

INTRODUCTION

Considerable research interest has been generated recently in the superior extracting ability of complex metal anions by high-molecular-weight quaternary ammonium bases. These bases, which are currently available in huge commercial quantities at low cost, are becoming very popular due to their promise for industrial chemical separations (*1*).

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Recent publications have appeared in the literature suggesting the quarternary ammonium base, Aliquat 336-S, for use in removing toxic metal ions such as mercury (*1*, *2*) and cadmium (*3*) from industrial waste water.

There are no minerals or ores found in nature with a high cadmium content. In nature, this highly toxic material is always found in trace quantities in zinc minerals and ores. Any industrial process for the removal of cadmium must take into account the huge excess of zinc.

In a recent paper (*4*), we described a new solvent extraction system for removal of zinc ions from aqueous iodide solution. Although the Aliquat 336-S-iodide extraction system was effective for the removal of both the zinc and cadmium ions from aqueous solutions, it has several disadvantages for serious considerations for industrial applications. The iodide is easily oxidized to iodine which renders the solutions dark and increases the quantity of iodide, which must be added to the solution for quantitative separation. Another disadvantage is the high cost of the hydroiodic acid used in the system. This led us to our investigation of the Aliquat 336-S-bromide system for the removal of zinc ions described in this communication.

EXPERIMENTAL

Apparatus

A NaI(Tl) well-type gamma scintillation counter, 1.75 × 2.0 in., consisting of a high-voltage power supply, a discriminator, and a timer scaler was used for gamma counting. A Sargent NX digital pH meter was used to make the pH measurements. High-speed motors equipped with glass paddle stirrers were used to mix the phases.

Reagents

Aliquat 336-S (impure tricaprylammonium chloride) is a quaternary amine chloride available from General Mills, Inc., Kankakee, Illinois. A 30% Aliquat 336-S-Cl stock solution was prepared by dilution with reagent grade xylene. The amine chloride was converted to the bromide by the method described by Moore (*2*).

Tracers, ^{109}Cd and ^{65}Zn, were obtained from New England Nuclear Corporation, Boston 18, Massachusetts. All other chemicals were reagent grade.

Evaluation Procedure

Five milliliters of the indicated aqueous phase containing approximately 1 × 10^5 gamma counts per minute of ^{65}Zn were extracted at room temperature with an equal volume of Aliquat 336-S-Br-xylene in 50-ml heavy-duty glass centrifuge tubes for 3 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 then analyzed for ^{65}Zn by counting 1-ml aliquots in culture tubes with a well-type gamma scintillation counter.

RESULTS

Aliquat 336-S-Br and its salt with the bromo complex of zinc are essentially insoluble in aqueous solutions but show high solubility in most common organic solvents.

The pertinent variables of the zinc-Aliquat 336-S-Br extraction system were investigated by use of the evaluation procedure previously described. Each solution studied contained 1 mg/ml zinc as zinc bromide unless otherwise specified.

A minimum of approximately 3% Aliquat 336-S-Br is required for quantitative removal of the zinc in an equal volume aliquot of a solution which is 1 mg/ml in zinc and 1.0 *M* in HBr. There was no measureable extraction observed when attempts were made to extract zinc from aqueous bromide solutions with pure xylene or xylene which had been treated with 1.0 *M* HBr. A 5% Aliquat 336-S-Br-xylene solution was used in the later investigations.

The extractions of zinc with 5% Aliquat 336-S-Br-xylene as a function of HBr concentration (Table 1) shows that a relatively high HBr concentration (about 0.5 *M*) is required to remove the zinc essentially quantitatively from aqueous bromide solutions with a single extraction.

The effect of pH on the extractability of zinc is closely related to the effect of HBr concentration. A solution at pH 1.0 containing approximately 10^{-2} *M* bromide, added with the carrier and HBr in adjusting the pH, is 97% extracted with Aliquat 336-S-Br-xylene. At a pH of 2.0, the percent extracted is reduced to 35. If, on the other hand, the aqueous solution is made 1.0 *M* in bromide with KBr, the percent extracted is increased to greater than 99.9% for both the pH 1.0 and pH 2.0 solutions. At a pH $\geqq$ 3, the percent extracted is reduced to essentially zero.

TABLE 1

Extraction of Zinc as a Function of HBr Concentration[a]

HBr concentration (M)	Zinc extracted (%)
0.4	99.0
0.6	>99.9
0.7	>99.9
1.05	>99.9
1.4	>99.9

[a] Initial aqueous solution contained 1 mg/ml Zn. Solvent, 5% Aliquat 336-S-Br-xylene.

Equilibrium is achieved very rapidly; a mixing period of only 15 sec proved to be adequate for essentially quantitative extraction. Three-minute extraction periods were used in the evaluation prodecure.

Several aqueous reagents (Table 2) were evaluated to determine their ability to strip zinc from 5% Aliquat 336-S-Br-xylene solutions. The organic phase, initially containing 1 mg/ml zinc as the bromo-zinc complex salt of Aliquat 336-S-Br, was stripped for 5 min with equal volume portions of the various strippants. All the strippants investigated stripped the zinc substantially, with the majority removing more than 99% of the element from the organic phase. Those strippants removing more than 99% of the zinc include Na_2SO_3 ($\geqq$ 1.0 M), NaOH ($\geqq$ 0.5 M), NH_3 ($\geqq$ 0.1 M), ethylenediamine ($\geqq$ 0.3%), and EDTA ($\geqq$ 0.5%).

DISCUSSION

The mechanism of extraction of zinc from aqueous bromide solutions with Aliquat 336-S-Br is of the type:

$$Zn^{2+} + 4Br^- \rightleftarrows ZnBr_4{}^{2-}$$

$$2[R_4NBr]_o + [ZnBr_4]_a{}^{2-} \rightleftarrows [(R_4N)_2ZnBr_4]_o + 2Br_a{}^-$$

where $[R_4NBr]$ is the Aliquat 336-S-Br, o is the organic phase, and a is the aqueous phase.

Since extraction studies have been made of the Aliquat-336-S-I-xylene system in aqueous iodide solution (*4*), this investigation of the aqueous bromide system affords an opportunity to compare the two systems.

A higher concentration of iodide is required to quantitatively remove the zinc from solution in the iodide system than the quantity of bromide required in the bromide system. An iodide concentration of 1.0 M is needed

TABLE 2

Stripping of Zinc from 5% Aliquat 336-S-Br-Xylene Solutions

Strippant		Zinc stripped (%)
Na_2S-M	1.0	88.3
	2.0	96.0
Na_2SO_3-M	0.1	49.0
	0.5	95.5
	1.0	>99.9
NaOH-M	0.1	53.6
	0.5	>99.9
NH_4OH-M	0.05	81.9
	0.1	>99.9
	0.5	>99.9
EDA-%	0.15	91.4
	0.2	96.9
	0.3	>99.9
	0.6	>99.9
	1.0	>99.9
	2.5	>99.9
	5	>99.9
EDTA-%	0.1	74.2
	0.5	98.5
	1.0	99.5

whereas a bromide concentration of only 0.5 *M* is sufficient in the bromide system. Zinc cannot be extracted from neutral or alkaline solutions using either the iodide or bromide systems, even with a large excess of iodide (as KI) or bromide (as KBr).

The bromide system differs from the iodide in that only a 15-sec mixing time is needed for essentially quantitative separation whereas at least 2 min are required for the iodide system. Larger aqueous phase to organic phase ratios can be used for extraction when using the bromide system than when using the iodide.

Higher concentrations of each strippant are required to strip the zinc from 5% Aliquat 336-S-Br-xylene than are required to remove the zinc from 5% Aliquat 336-S-I-xylene. These results clearly indicate that the complex salt formed by the interaction of the tetrabromozincate(II) anion with Aliquat 336-S-Br is more stable than the salt formed with Aliquat 336-S-I. It would appear from these observations that $ZnBr_4^{2-}$ is more stable than ZnI_4^{2-}. This stability trend is the reverse of that found with the tetrahalo complexes of mercury ($H_gI_4^{2-} > H_gBr_4^{2-}$). Both complexes of zinc are very unstable when compared to the corresponding mercury complexes. In fact, there is some question on the existence of the tetrahalo complexes of zinc in aqueous solution (*5*). Our investigations add supportive evidence of their existance.

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