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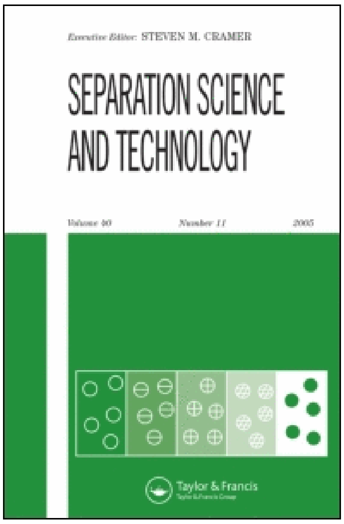

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Solvent Extraction Studies of Zinc and Cadmium with Aliquat 336-S in Aqueous Chloride Solutions

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NOTE

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Abstract

New solvent extraction systems have been developed for the extraction of zinc and cadmium from aqueous chloride solution using Aliquat 336–S dissolved in the nonpolar solvents heavy aromatic naphtha and xylene as the extractant. Moderately high concentrations of the metal ions (1 mg/ml zinc and 2 mg/ml Cd) can be extracted quantitatively from acid solutions with an equal volume of 5% Aliquat 336–S solution in 15 sec. Both zinc and cadmium can be stripped from the organic phase with a series of aqueous stripping solutions. When comparing zinc and cadmium, cadmium is the easier to extract and the more difficult to strip under the same experimental conditions.

INTRODUCTION

Several investigators have reported that both zinc and cadmium can be quantitatively extracted from aqueous halide solutions using high-molecular-weight quaternary ammonium bases (often called quaternary amines) (*1–5*). Comprehensive studies have been undertaken of the various parameters associated with the optimum extraction of zinc in aqueous iodide (*4*) and bromide (*5*) solutions using the quaternary amine Aliquat 336-S. Similar studies have been made on mercury in chloride (*6*), mercury in

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*Taken in part from the thesis of Ta-Sheng Lin submitted to the Graduate School for the Master of Science Degree.

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iodide (*7*), and cadmium in iodide (*3*) media. These investigations have led to the development of periodic trends in the Group IIB and halogen families for the various tetrahalo–quaternary amine systems. Pribil and Vesley (*2*) recently reported an extraction procedure using Aliquat 336-S for zinc and cadmium in chloride and iodide media. Their study led to an excellent complexometric method for the determination of each metal in the presence of each other and other foreign metal ions. Their study did not include a comprehensive investigation of the variables as reported for the other metal halide–amine systems in the aforementioned investigations.

We have conducted a study of the extraction of zinc and cadmium in aqueous chloride solutions with Aliquat 336-S in order to correlate our findings with the other Group IIB metal–halide systems to determine the periodic trends.

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EXPERIMENTAL

Apparatus

A NaI (TI) well-type scintillation counter, 1.75 × 2.0 in., consisting of a high voltage power supply, a discriminator, and a timer scaler, was used for the gamma counting. 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

Aliquat 336-S (impure trioctylmethylammonium chloride) is a quaternary ammonium base available from General Mills, Inc., Kankakee, Illinois. For the cadmium investigations a 30% (v/v) Aliquat 336-S 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. Due to the shortage of xylene as a result of the energy crisis, heavy aromatic naphtha (HAN) was substituted as a solvent for xylene in the zinc investigations. HAN is an aromatic fraction from crude oil distillation consisting primarily of hydrocarbons with nine to twelve carbons and a boiling range of about 170 to 260°C. HAN is available from all oil companies in huge industrial quantities, and it is also available from many of the chemical supply houses. The Aliquat 336-S–HAN solutions were prepared and used the same as in the case of the xylene solutions.

Cadmium-109 and zinc-65 tracers were obtained from New England Nuclear Corporation, Boston 18, Massachusetts. Deionized water was used in all the investigations.

Evaluation Procedure

Five millimeters of the indicated aqueous phase containing approximately 1×10^4 gamma counts per minute per milliliter of ^{65}Zn or ^{109}Cd were extracted at room temperature with an equal volume of 5% Aliquat 336-S–xylene in 50 ml heavy duty 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 or ^{109}Cd by counting 1 ml aliquots in culture tubes with a well-type gamma scintillation counter.

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RESULTS

Aliquat 336-S and its salts with the tetrahalo complexes of zinc and cadmium are essentially insoluble in aqueous solutions, but show very high solubilities in most common nonpolar solvents such as xylene, kerosene, and benzene. Xylene and HAN were chosen for our investigations, both of which proved entirely satisfactory. HAN has the advantage of a higher boiling range which means less loss due to evaporation since the extractions are carried out in open centrifuge tubes. HAN also has the advantage of being less expensive.

The pertinent variable of the zinc–Aliquat 336-S and cadmium–Aliquat-336-S systems were investigated by use of the evaluation procedure previously described. Each solution studied contained 1 mg/ml zinc as zinc chloride or 2 mg/ml cadmium as cadmium chloride unless otherwise specified. The 1 mg/ml and 2 mg/ml concentrations for zinc and cadmium were chosen in order to make the cadmium and zinc concentrations about equal on a molar basis and yet use the simpler concentration units. In addition, other published investigations of similar cadmium and zinc systems used these concentrations. This makes correlation of our data with that already in the literature much easier.

A 3% solution of Aliquat 336-S proved adequate for the quantitative removal of the zinc in an equal volume aliquot of solution which is 1 mg/ml in zinc and 1.0 *M* HCl with a single extraction. A 3% solution also proved sufficient to quantitatively extract the cadmium from a solution which is 2 mg/ml in cadmium and 1.0 *M* in HCl. There was no measurable extraction observed when attempts were made to extract zinc or cadmium from aqueous chloride solutions with pure xylene, HAN, or these two solvents treated with 1.0 *M* HCl. A 5% Aliquat 336-S solution was chosen to be used in further investigations of both zinc and cadmium systems.

A very small HCl concentration is needed for removal of both zinc and cadmium from aqueous chloride solution. More than 98% of the zinc is removed from a 0.03 *M* HCl solution. Cadmium is quantitatively removed from aqueous solutions containing as little as 10^{-2} *M* HCl.

The effect of pH on the extractability of both zinc and cadmium is closely related to the effect of HCl concentration. Over 99% of the cadmium is extracted from acidic solution with a pH up to 7, whereas only 89% of the zinc is extracted at a pH of 7. The degree of extraction falls rapidly for both cadmium and zinc at pH values above 7. At a pH of 10.1, 81% of the cadmium is extracted, whereas at a pH of 7.5 only 66% of the zinc is extracted. At a pH of 10, if the solution is made 1.0 *M* in chloride as NaCl, more than 95% of zinc and cadmium can be extracted. The ligands, thiocyanate, cyanate, and cyanide can be substituted for the excess chloride, and in each case more than 95% of the two metals can be extracted at a pH of 10.

Equilibrium is achieved rapidly for both the zinc and cadmium systems; a mixing period of only 15 sec proved to be sufficient for essentially quantitative extractions. Three-minute extraction periods were arbitrarily chosen for use in the evaluation procedure.

TABLE 1

Stripping of Zinc from 5% Aliquat 336-S-HAN Solutions

Strippant		Zinc stripped (%)
Na_2S (*M*)	1.0	58.07
Na_2SO_3 (*M*)	1.0	44.60
NaOH (*M*)	1.0	96.91
NH_4OH (*M*)	0.1	96.72
	0.5	96.61
	1	96.93
	2	97.74
EDA (%)	1	97.81
	2.5	97.89
	5	98.53
EDTA (*M*)	0.1	89.83

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TABLE 2

Stripping of Cadmium from 5% Aliquat 336-S-Xylene Solutions

Strippant		Cadmium stripped (%)
Na_2S (*M*)	1.0	0.41
Na_2SO_3 (*M*)	1.0	46.46
NaOH (*M*)	1.0	26.65
NH_4OH (*M*)	0.1	47.31
	0.5	98.20
	1.0	99.39
	2.0	98.89
EDA (%)	1.0	99.11
	2.5	98.83
	5.0	99.15
EDTA (*M*)	0.1	90.22

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A group of reagents were evaluated to determine their ability to strip zinc (Table 1) and cadmium (Table 2) from 5% Aliquat 336-S solutions. The zinc stripping solution contained 1 mg/ml zinc as the tetrachloro-zinc complex salt of Aliquat 336-S in the organic phase. The cadmium stripping solution contained 2 mg/ml cadmium as the tetrachloro-cadmium complex salt of Aliquat 336-S. The stripping solutions were stripped for 3 min with equal volume proportions of the various strippants. The majority of the strippants investigated stripped both zinc and cadmium substantially, usually greater than 95%. A sodium sulfide solution stripped 58% of the zinc, whereas it strips less than 1% of cadmium. Sodium hydroxide strips 97% of the zinc but only 27% of the cadmium.

Cadmium can be quantitatively extracted with aqueous phase to organic phase ratios of up to 20 to 1. At this ratio only 87% of the zinc is extracted.

DISCUSSION

The mechanism of extraction of zinc and cadmium from aqueous chloride solutions with Aliquat 336-S is of the type:

$$M^{+2} + 4Cl^- \rightleftarrows MCl_4{}^{2-}$$

$$2[R_4NCl]_o + [MCl_4]_a{}^{2-} \rightleftarrows [R_4NMCl_4]_o + 2Cl_a{}^-$$

where R_4NCl is Aliquat 336-S, "o" is the organic phase, and "a" is the aqueous phase.

The study of the extraction of zinc and cadmium with Aliquat 336-S in chloride media enables us to further develop periodic trends in the Group IIB and halogen families. This enables us to directly compare the zinc chloride system with the zinc bromide (*4*) and the zinc iodide (*5*) systems. It also affords the opportunity to compare the cadmium chloride with the mercuric chloride (*6*) and zinc chloride systems.

In comparing the cadmium chloride system with the zinc chloride system, one observes that cadmium can be quantitatively extracted at a lower HCl concentration and consequently at a higher pH. Cadmium can be extracted quantitatively from solutions with large aqueous phase to organic phase ratios, whereas zinc is only partially extracted. Two strippants, notably sodium sulfide and sodium hydroxide, strip zinc substantially and cadmium very little. These observations lead one to conclude that it is easier to extract cadmium and more difficult to strip the tetrachloro–cadmium complex salts of Aliquat 336-S than the corresponding complexes of zinc. Comparing our results with those of Moore (*6*) for the mercuric chloride system, the order of decreasing difficulty in extractions is Hg, Cd, Zn. In aqueous chloride solution these metals occur as the tetrahalo metal complexes $HgCl_4{}^{2-}$, $CdCl_4{}^{2-}$, and $ZnCl_4{}^{2-}$. The order of decreasing formation constants is $HgCl_4{}^{2-} > CdCl_4{}^{2-} > ZnCl_4{}^{2-}$. The constants for cadmium and mercury are accurately known. The formation constant for the zinc complex is not well established but it is much smaller than those for mercury and cadmium. It is noteworthy to point out that the ease of extraction is in the same order as the decreasing stabilities of the tetrahalo complexes. The obvious conclusion from these observations is that the more stable the tetrahalo metal complexes, the easier it is to extract the metal and the more difficult it is to strip it from the organic phase.

The above observations are particularly useful for the zinc chloride, zinc bromide (*5*) and zinc iodide (*4*) systems. The formation constants for $ZnCl_4{}^{2-}$, $ZnBr_4{}^{2-}$, and $ZnI_4{}^{2-}$ are not well established. These complexes are very unstable when compared with the corresponding mercury and cadmium complexes in that their formation constants are several orders of magnitude smaller. There remains some question of the existance of some of the tetrahalo–zinc complexes. The complex $ZnCl_4{}^{2-}$ has definitely been characterized since it has been isolated as a salt with the hexaamine cobalt(III) cation (*8*).

In comparing the three zinc systems, the chloro complex is the easiest to extract followed by the bromo and the iodo complexes. The reverse trend was observed for the stripping investigations. From these observations we concluded that the order of decreasing stabilities of the complexes is $ZnCl_4^{2-}$

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$> ZnBr_4^{2-} > ZnI_4^{2-}$. It is noteworthy to point out the reverse order of the stabilities of the tetrahalo mercurate(II) anions. The same order has been suggested by Cotton and Wilkerson (*9*), although there was great uncertaintity of the actual values of the constants.

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