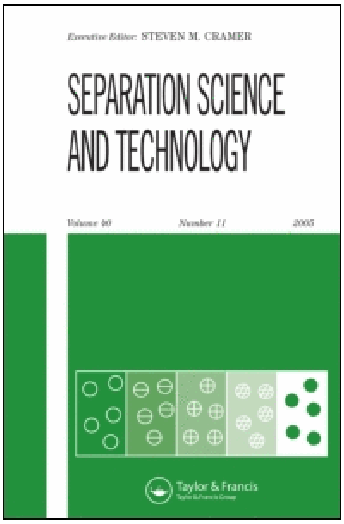

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Liquid–Liquid Extraction of Mercury with High-Molecular-Weight Amines from Iodide and Bromide Solutions*

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Abstract

New systems are described for the highly efficient solvent extraction of mercury with high-molecular-weight amines from aqueous iodide or bromide solutions. Mercury extracts essentially quantitatively at both the subnanogram and macro levels. The quaternary amines are especially attractive because of their ability to extract mercury from alkaline as well as acidic solutions. Regeneration of the amine solvent is readily achieved by stripping the mercury with alkaline solutions of cysteine.

INTRODUCTION

Solvent extraction with high-molecular-weight amines is a promising technique for attacking some of the industrial pollution problems of mercury and other toxic metals. In a recent paper (*1*) we described a new system for the removal of mercury from brine solutions with these reagents. As part of a program to lay the groundwork for the development of practicable methods for toxic metal abatement processes, the extraction of mercury in the iodide and bromide systems is now discussed. Solvent extraction of mercury with amines in these systems has not been reported previously.

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EXPERIMENTAL

Apparatus

A NaI(Tl) well-type scintillation counter, 1.75 × 2 in., was used for gamma counting.

Reagents

Primene JM-T is a mixture of primary amines, principally in the C_{18-22} range.

Primene 81-R is a mixture of primary amines, principally in the C_{12-14} range.

Amberlite LA-1 (*N*-dodecenyltrialkylmethylamine) is a secondary amine. This secondary amine and the primary amines listed above are available from Rohm and Haas Co., Philadelphia, Pennsylvania.

Alamine 336-S (tricaprylamine) is a tertiary amine available from General Mills, Inc., Kankakee, Illinois.

Aliquat 336-S (tricaprylmethylammonium chloride) is a quaternary amine chloride available from General Mills.

Adogen 464, methyl tri (C_8–C_{10}) ammonium chloride is a quaternary amine chloride available from Archer Daniels Midland Co., Minneapolis, Minnesota.

The amines were dissolved in reagent grade xylene or diethylbenzene. The amines were converted to the iodide salts by the following pretreatment: equal volume portions were extracted twice for 5 min each with 10% Na_2CO_3 followed by three 5-min extractions with 6 *M* KI. The solutions were centrifuged for 5 min after the last treatment and the organic phase was used in the various studies. A similar procedure was used to prepare the bromide salts using 8.7 *M* HBr.

Mercury-203 tracer is available from New England Nuclear Co., Boston, Massachusetts.

All other chemicals were reagent grade.

Evaluation Procedure

Five milliliters of the indicated aqueous phase containing 1 × 10^5 gamma counts/min/ml of ^{203}Hg tracer was extracted at room temperature with an equal volume portion of the various solvents in 50-ml heavy duty glass centrifuge tubes. Three minute mixing periods were selected arbitrarily. High-speed motor stirrers equipped with glass paddles were used for the extractions. After extraction, the tubes were centrifuged in a clinical centrifuge for 2 min. Each phase was then analyzed for mercury-203 by counting 1-ml aliquots in a well-type gamma scintillation counter.

RESULTS AND DISCUSSION

The mechanism of extraction of mercury from aqueous iodide or bromide solutions with a quaternary amine is of this type:

$$Hg^{2+} + 4X^- \rightleftharpoons (HgX_4)^{2-}$$

$$2(R_4NX)_o + (HgX_4)_a^{2-} \rightleftharpoons [(R_4N)_2HgX_4]_o + 2X_a^-$$

where X = iodide or bromide, R_4NX = Aliquat 336-S-X or Adogen 464-X, o = organic phase, and a = aqueous phase.

The quaternary amine and its salt with the anionic halo complex of mercury are essentially insoluble in aqueous solutions but exhibit high solubility in organic solvents.

THE IODIDE SYSTEM

The iodide ion is one of the strongest inorganic complexers of mercury. The anionic iodo mercuric complex is highly stable in both acidic and alkaline solutions. Mercury does not precipitate even at rather high alkalinities in the presence of the iodide ion. Quaternary amines dissolved in suitable solvents can extract the anionic species of mercury efficiently from both alkaline and acidic aqueous solutions.

The pertinent variables were studied by use of the procedure described above. The extraction of mercury (Table 1) with 5% Aliquat 336-S-I-

TABLE 1

Extraction of Mercury with 5% Aliquat 336-S-I-Xylene from Iodide Solutions

Initial aqueous phase	Hg extracted (%)
0.06–4.7 *M* HI 2 mg/ml Hg	>99.9
0.06 *M* HI, pH range = 1.3–12.5 2 mg/ml Hg	>99.9

xylene is quantitative from dilute to concentrated solutions of hydriodic acid and from alkalinities as high as pH 12.5. The behavior of ^{203}Hg tracer (<1 μg/ml) appeared to be identical to that of mercury at the 2 mg/ml level, showing quantitative extraction from aqueous solutions containing as high as 5.9 *M* potassium iodide.

Equilibrium is reached rapidly in this system; a 0.5-min mixing period is adequate.

The extraction of mercury as a function of Aliquat 336-S-I concentration in xylene is shown in Table 2. Initial aqueous phases contained 2 mg/ml mercury, 1×10^5 gamma counts/min/ml of ^{203}Hg tracer, and 0.26 *M* potassium iodide. Extractions were performed for 3 min with equal volume portions of the solvent. Extraction of mercury is quantitative, provided the quaternary amine:mercury molar ratio is $\gtrsim 2$.

The extraction of mercury from 0.26 *M* potassium iodide solutions as a function of amine class is shown in Table 3. The quaternary amines are superior extractants to the other classes of amines at high pH's. Several additional experiments with the primary, secondary, and tertiary amines indicated that they were efficient extractants for mercury from acidic iodide solutions provided the aqueous pH was $\lesssim 5$. Detailed studies on these reagents were not done because the quaternary amines were excellent mercury extractants from both alkaline and acidic solutions.

In all cases diethylbenzene was as satisfactory as xylene as a diluent

TABLE 2

Extraction of Mercury as a Function of Aliquat 336-S-I Concentration in Xylene

Concentration of Aliquat 336-S-I in xylene (%)	Hg extracted (%)
0.01	<1.0
0.05	10.6
0.10	20.0
0.2	41.1
0.3	59.1
0.5	87.9
1.0	>99.9
2.0	>99.9
3.0	>99.9
5.0	>99.9

TABLE 3

Extraction of Mercury from 0.26 *M* Potassium Iodide as a Function of Amine Class

Amine extractant in xylene	Class	Hg extracted (%)
5% Primene JMT	Primary	29.3
5% Primene 81R	Primary	60.3
5% LA-1	Secondary	7.5
5% Alamine 336-S	Tertiary	23.1
5 Aliquat 336-S-I	Quaternary	>99.9
5% Adogen 464-I	Quaternary	>99.9

for the amines. The quaternary amine, Adogen 464, gave results essentially identical to those obtained with Aliquat 336-S throughout the studies.

STRIPPING OF MERCURY FROM THE QUATERNARY AMINE SOLVENT

Because of the remarkable stability of the mercuric iodo complex in the organic solvent, few reagents are effective strippants for mercury. Considerable work was done on this aspect of the system. Numerous aqueous stripping agents were evaluated for their ability to strip mercury from 5% Aliquat 336-S-I-xylene solutions. The organic solvents initially containing 2 mg/ml mercury were stripped by extracting for 3 min with equal volume portions of the various aqueous strippants.

Negligible stripping (<1%) of mercury from the solvent was effected with dilute to concentrated solutions of sodium hydroxide, ammonium hydroxide, sodium sulfite, sodium thiosulfate, sulfuric acid, perchloric acid, various oxidizing and reducing agents, and aluminum turnings. The chelating agents, glycine, diethyldithiocarbamate, and (ethylenedinitrilo) tetraacetic acid were also ineffective mercury strippants.

The few promising strippants found are shown in Table 4. Nitric acid at high concentrations stripped the mercury but some degradation of the solvent occurred. Dilute solutions of ethylenediamine (EDA) were completely ineffective. Interestingly, by contrast 2.5% ethylenediamine strips mercury quantitatively from the same solvent in the chloride system (*1*). By the use of high concentrations of ethylenediamine, it is possible to strip mercury appreciably from the quaternary amine iodide solvent. Also, by lowering the quaternary amine concentration in the solvent, efficient stripping of mercury is possible. Thus 70% ethylenediamine stripped 97% of the mercury from 1% concentrations of the quaternary amine iodide solvent.

Further studies revealed that cysteine, a well-known mercury complexer, was by far a superior strippant for mercury in the quaternary amine–iodide system. Alkaline aqueous solutions of cysteine stripped mercury quantitatively from the solvent. Mechanical behavior and material balances were excellent at both the macro and tracer levels.

Experiments were performed to determine if the more active metal, aluminum, could be used to reduce and precipitate mercury directly from the organic iodide solvent. Preliminary tests on the reduction of mercury from 0.26 *M* potassium iodide solutions indicated excellent reduction with aluminum (Table 5). Five milliliter portions of 0.26 *M* potassium iodide aqueous solutions containing 2 mg/ml mercury were mixed for varying periods of time with 2.3 g of aluminum turnings. The reduction–precipitation of mercury in the aqueous solution is essentially complete in 1 hr.

Identical experiments were done with the mercury initially contained in 5% Aliquat 336-S-I-xylene solutions. Negligible reduction (<1%) of the mercury was effected, even after contact periods of 18.5 hr. These results show a drastic difference from those found in the analogous chloride system (*1*), in which efficient reduction–precipitation was

TABLE 4

Stripping of Mercury from 5% Aliquat 336-S-I-Xylene Solutions

Strippant	Hg stripped (%)
HNO_3 *M*, 5	1.9
10	29.1
12	98.6
Na_2S, 1 *M*	65.2
Ethylenediamine, 2.5%	<1.0
20%	<1.0
50%	2.9
70%	51.3
0.1 *M* L-cysteine·HCl in H_2O	<0.1
0.1 *M* L-cysteine·HCl–1 *M* NaOH	>99.9
0.1 *M* L-cysteine·HCl–0.1 *M* NaOH	>99.9
0.1 *M* L-cysteine·HCl–5% ethylenediamine	>99.9

TABLE 5

Reduction-Precipitation of Mercury from 0.26 *M* Potassium Iodide Solution

Reduction time (min)	Hg reduced (%)
10	46.1
25	86.1
60	98.3
135	99.4

achieved from the quaternary amine chloride solvent. These reduction studies again illustrate the great strength of the mercuric iodo complex in the amine solvent.

Although the extraction and subsequent stripping of mercury in the amine iodide system is quantitative, it was of practical interest to determine the utility of the regenerated solvent in a second cycle extraction of mercury. The feed solution contained 0.1 *M* potassium iodide, 2 mg/ml mercury, and ^{203}Hg tracer (1 × 10^5 gamma counts/min/ml). Twenty-five milliliters of the feed solution was extracted for 3 min with 25 ml of 5% Adogen 464-I-xylene. The mercury was then stripped from the solvent by extracting for 3 min with 25 ml of 0.1 *M* cysteine–5% ethylenediamine. The regenerated solvent was then used in a second cycle to extract fresh portions of the potassium iodide feed solution. Mercury recovery was quantitative ($>$99.9%) throughout the two cycle process. The alternate strippants, 0.1 *M* cysteine–1 *M* NaOH or 0.1 *M* cysteine–0.1 *M* NaOH, provided essentially identical behavior to that described above. Mercury forms a very strong soluble complex with cysteine in alkaline solution, thereby favoring quantitative stripping with excellent mechanical behavior.

Further experiments revealed that tracer mercury ($<$1 μg/ml) behaved the same as macromercury in the two cycle process.

THE BROMIDE SYSTEM

A brief investigation of the extraction behavior of mercury with a tertiary and quaternary amine in the bromide system was made. From aqueous solutions containing 0.2–7.0 *M* HBr, mercury extracted $>$99.9% at both the tracer and macro (2 mg/ml) levels with equal volume portions of either 5% Alamine 336-S-xylene or 5% Adogen 464-Br-xylene in 3-min. mixing periods.

As expected, the tertiary amine, Alamine 336-S, was an ineffective extractant from alkaline bromide solutions. The quaternary amine, Adogen 464, extracted mercury efficiently from aqueous bromide solutions up to pH ~12.

At the 2 mg/ml level mercury stripped essentially quantitatively from 5% Alamine 336-S-xylene in 3 minutes with equal volume portions of 2.5% EDA, 1 *M* NaOH, or 5 *M* NH_4OH. These reagents were ineffective strippants for mercury from the stronger 5% Adogen 464-Br-xylene solvent; however, 30% EDA stripped 93% mercury from this quaternary amine bromide.

Applications

The high-molecular-weight amines are excellent extractants for mercury from iodide or bromide solutions. These reagents offer new tools for the isolation, recovery, and pollution abatement of mercury from various industrial and natural solutions. Especially attractive are the commercially-available quaternary amines, Adogen 464 and Aliquat 336-S, because they function in alkaline as well as acidic solutions. Thus mercury (10 mg/ml) does not precipitate from solutions containing as high as 5 *M* NaOH in the presence of 0.2 *M* KI. The soluble mercuric iodo complex quantitatively extracts from this highly alkaline solution with the quaternary amines. Moreover, it is easy to extract mercury quantitatively from aqueous solutions containing no iodide ion, provided the quaternary ammonium iodide solvent satisfies the required stoichiometry.

When one compares the above studies on the amine extraction and stripping behavior or mercury in the iodide and bromide systems to the previously reported chloride system (*1*), it is clear that the order of decreasing mercuric halide stability is iodide $\gg$ bromide $>$ chloride.

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