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Extraction and Preconcentration of Mercury(II) from Aqueous Solutions

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Abstract

The extraction/preconcentration of mercury(II) from aqueous media using diphenyl-2-pyridylmethane (DPPM) in benzene has been studied. The factors influencing the extraction are optimized. An extractive preconcentration procedure has been proposed on the basis of its quantitative extraction in a single equilibration from 1 *M* hydrochloric acid solution containing 0.02 *M* potassium thiocyanate. Extracted mercury can be stripped almost completely into 10 *M* aqueous solutions of hydrochloric or perchloric acid. A mechanism has been proposed, and the extractable species is assumed to be $HgCl_{2-n}(SCN)_n(DPPM)_2$, where $n = 1, 2$. Aqueous to organic volume ratios up to 100:1 can be used without loss of extraction efficiency, and the procedure can effectively be used in water pollution abatement studies.

INTRODUCTION

Mercury is one of the toxic elements which is being discharged into the environment from a variety of human activities (*1*). Through various natural and chemical processes it easily enters into living systems, causing mercury pollution. A large number of analytical techniques have been employed for the determination of this pollutant. The sensitivity of these techniques is generally improved by preconcentration with solvent extraction. It is, therefore, necessary to have rapid and simple methods which can isolate the metal quantitatively and selectively. The aim of this work

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was to develop a procedure for the separation/preconcentration of mercury from different matrices. The present paper deals with the extraction of mercury by DPPM which has been proved to be a useful extracting reagent for a number of elements in our laboratory (*2–5*).

EXPERIMENTAL

Reagents and Radiotracers

DPPM was used as an extractant as supplied by Aldrich Chemical Co., Milwaukee, Wisconsin, without any further purification. The characteristics of this reagent have been reported elsewhere (*2*). Benzene was used as a diluent. Standard solutions were used to prepare most of the acid solutions. All other chemicals employed in this work were either C.P. or AnalaR grade. Deionized and doubly distilled water was used in all the experiments. Radiotracers were either obtained from Radiochemical Centre, Amersham, England, or were prepared locally from neutron irradiation of spec-pure metals or their respective compounds in the research reactor PARR-I of this Institute at a thermal neutron flux of about 2×10^{13} n/cm^2 sec^1. Radiochemical separations were applied whenever necessary.

Instrumentation

Radiochemical purity of the tracers was checked by gamma spectrometry using a 30-cm^3 Ge(Li) detector in conjunction with a Nuclear Data Model ND-4410 computerized analyzer system. The gamma spectra were recorded with a Technical Measurement Corp. 100 channel analyzer, Gamma Scope II Model 102, coupled with a NaI(Tl) detector. Gross gamma measurements were made with Nuclear Chicago Model 8725 well-type scintillation counter using a 7.5 cm × 7.5 cm NaI(Tl) crystal. Beta activities were assayed with a G.E.C. tube Model EHM/2/S coupled with a Nuclear Chicago Model 8775 scaler. The activity of alpha emitters was determined with a Panex Reigate Series ARD/55/6 set up coupled with a windowless alpha-beta Anthracene (25 mm diameter) scintillator using a Nuclear Chicago alpha counter Model DS-S Serial 1709.

Extraction Procedure

Distribution studies were conducted at room temperature (24 ± 3°C). To 1 ml of HCl solution containing a tracer of mercury (^{203}Hg) or a test

element, KSCN was added to obtain the desired concentration. The concentration of mercury was always around 10^{-6} *M*. This solution was equilibrated with an equal volume of 0.1 *M* DPPM in benzene for 5 min. Preliminary investigations showed that equilibrium is established within 1 min. Two phases were separated by centrifugation, and the aliquots from each phase were assayed radiometrically. The distribution coefficient (*D*) was computed from the ratio of the total activity in the organic phase to that in the aqueous phase.

RESULTS AND DISCUSSION

The partition behavior of mercury(II) was first investigated as a function of the acid concentration using a 0.1 *M* DPPM solution in benzene. The results are shown in Fig. 1 (Curve 1). It is seen from the plot that the extraction efficiency varies with the concentration of hydrochloric acid and increases considerably with the increasing acid concentration, having a maximum at around 1 *M* concentration. A further increase in the acidity of the aqueous phase leads to a drastic decrease in the extraction such that in concentrated acid solutions most of the metal stays in the aqueous phase. The increase in the extraction with increasing aqueous hydrogen ion concentration is evidently due to a decrease in the activity of water and formation of less hydrolyzed and more extractable metal complexes of the type $Hg(OH)_{2-n}Cl_n$ ($n = 1, 2$). The decrease above 1 *M* acid is either due to acid competition for the basic functional group or due to the formation of anionic chloride complexes which are not efficiently extracted.

The presence of linear and less basic thiocyanate ions in aqueous solutions has been found to increase the extraction of certain transition metals ions including mercury (*6*). In this study the effect of KSCN on the extraction can be visualized from Fig. 1 which depicts the *D* values at varying HCl concentrations with and without 0.02 *M* KSCN. The comparison of the curves (Fig. 1) leads to the conclusion that the addition of KSCN to HCl solutions enhances the extraction of the metal without changing the general pattern of the partition behavior. Mercury(II) is extracted quantitatively (>99%) into 0.1 *M* DPPM in benzene from 1 *M* HCl solution containing 0.02 *M* KSCN in only a single equilibration. However, from moderate and high acid concentrations the extraction is not so efficient from either pure acid solutions alone or those containing SCN^-. This is because anionic chloride complexes of mercury(II) predominate in the aqueous solutions at relatively high acid concentrations, and this pyridine, due to its low basicity (*2*), does not result in the forma-

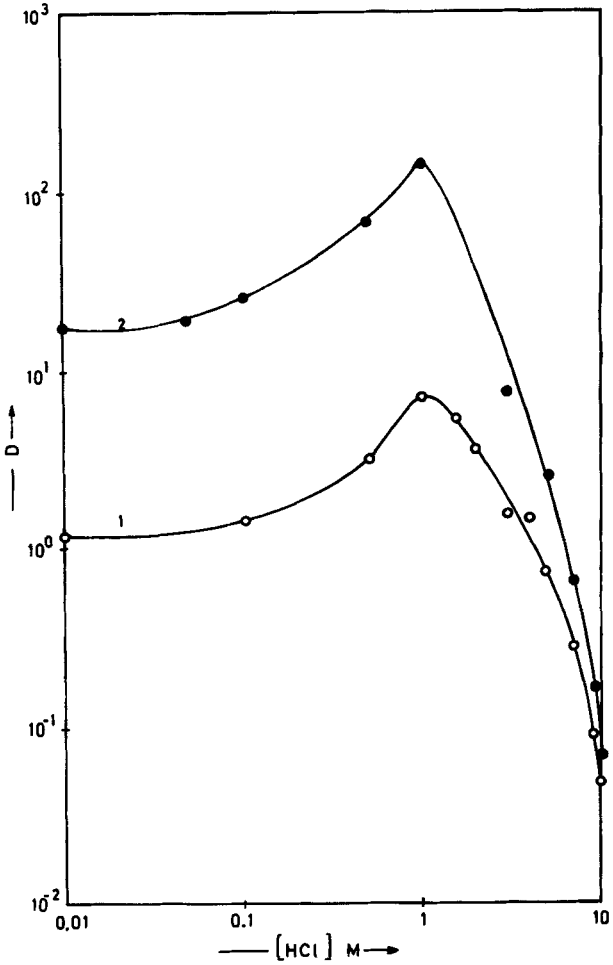

FIG. 1. The partition behavior of mercury(II) as a function of aqueous hydrochloric acid concentration. (1) HCl and (2) HCl solutions containing 0.02 *M* KSCN.

tion of stable cations of the type $(DPPMH)^+$ which may extract the anionic complexes through ion-pair mechanism.

The dependence of mercury extraction on potassium thiocyanate concentration (0.01 to 1 *M*) was examined from various fixed acid concentrations. Figure 2 shows the plots of distribution coefficients of the metal against KSCN concentrations in the aqueous phase, keeping the DPPM concentration (0.1 *M*) constant. The influence of KSCN concentration is significant, and its increase in the aqueous phase generally enhances the extraction. At low acid concentrations the addition of KSCN in the aqueous phase (up to 0.1 *M*) does not influence the distribution, but at

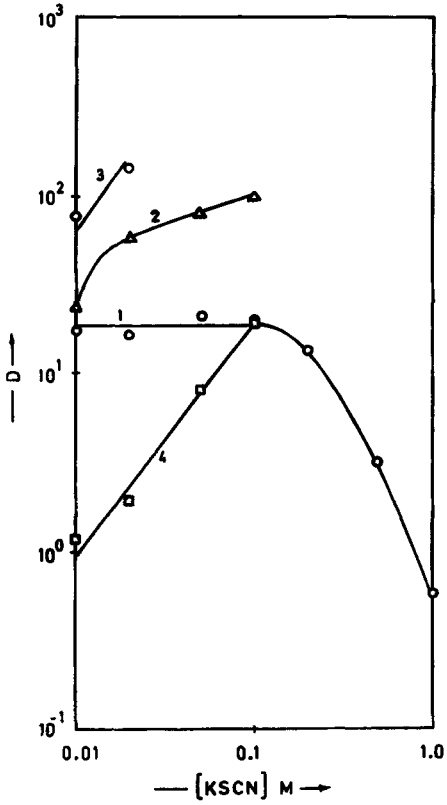

FIG. 2. The dependence of extraction of mercury(II) on the concentration of KSCN in aqueous HCl solutions. (1) 0.01 *M*, (2) 0.1 *M*, (3) 1 *M*, and (4) 5 *M*.

relatively higher concentrations the extraction decreases. Moreover, precipitation was observed in 0.1 and 5 *M* HCl solutions containing more than 0.1 *M* KSCN. A similar phenomenon was noticed with the addition of more than 0.02 *M* KSCN only to 1 *M* HCl solution. In relatively more concentrated acid solutions where the activity of water is considerably decreased, the increase in extraction is primarily due to the increased formation of neutral and hydrophobic thiocyanate metal complexes. The precipitation in dilute and moderate acid solutions indicates that thiocyanate ions engage the metal almost completely, leading to the anionic metal thiocynanate of the type $HgCl_{4-n}(SCN)_n$ (where $n = 3, 4$), and the solvent in the absence of extractable complexes and in the presence of free acid leads to the formation of the hydrochlorides (DPPM·HCl) which condensate to such an extent that micelles of the solvent salts settle down in the aqueous phase as precipitates. The condensation of chloride salts of alkyl-substituted pyridines has been reported in previous articles (*7*, *8*). However, in very dilute acid there is no precipitation above 0.1 *M* KSCN concentration, and the *D* value does not increase but decreases instead. This suggests that the metal ion is hydrated, and thiocyanate ions alone (with very weak acid) are not capable of eliminating the water molecules from the inner coordination sphere and instead get attached to the H^+ ion of the strongly polarized water molecules in the first or second hydrate shell, leading to negatively charged hydrated species whose extraction through anionic consequent at such low acidities is unlikely to happen.

Since the extraction is expected to be influenced by the reagent concentration, the variation of the distribution coefficient as a function of DPPM concentration (0.005 to 0.1 *M*) was also examined from aqueous 1 *M* hydrochloric acid containing 0.02 *M* KSCN. Figure 3 demonstrates a linear dependence of log *D* against log [DPPM] with a slope of around 2. This suggests that two molecules of the pyridine combine with one metal ion. The linear plots of the curves obtained from the dependence of thiocyanate ions show a slope of around 1.5, and thus in dilute and moderate acid solutions the extraction of the mixture of $Hg(SCN)_2(DPPM)_2$ and $HgCl(SCN)(DPPM)_2$ is indicated, and the extraction can be represented as

$$Hg(Cl)_{2-n}(SCN)_n + 2DPPM \rightleftarrows HgCl_{2-n}(SCN)_n(DPPM)_2$$

Several anions (acetate, borate, citrate, fluoride, iodide, oxalate, phosphate, tartrate, and thiosulfate) were added to the extraction system as their sodium salts to determine their effect on the extraction of mercury. The results given in Table 1 indicate that the extraction is not hindered at

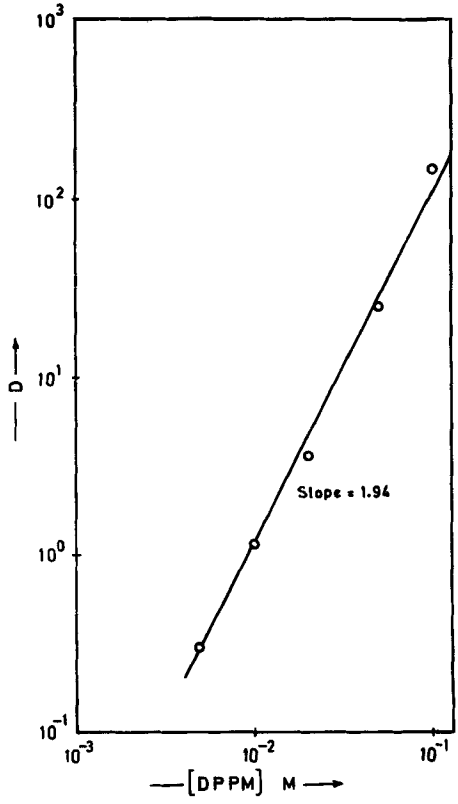

FIG. 3. The plot of D_{Hg} against DPPM concentration.

all by any of the anions tested at the concentrations typically found in the environmental samples, except in the cases of fluoride and phosphate where extraction is very slightly depressed. This indicates that these ions do not affect the extraction procedure. In addition, a few experiments were also carried out to study the stripping of mercury into the aqueous phase, and it was found that equal volumes of 10 *M* solutions of hydrochloric or perchloric acid can be utilized to strip more than 99% mercury from the organic phase in two to three equilibrations.

Distribution coefficients for a number of elements were determined under optimal conditions, and their separation factors with respect to mercury(II) were computed. These results are given in Table 2. The metal ions Cs(I), Mn(II), Sr(II), Ba(II), Sc(III), Cr(III), As(III), Eu(III), and

TABLE 1

Effect of Anions on the Extraction of Trace Amounts of Hg(II) ($\sim 10^{-6}$ *M*) with 0.1 *M* DPPM in Benzene from 1 *M* HCl Containing 0.02 *M* KSCN

Anion[a]	% extraction
Nil	>99
Acetate	99
Borate	99
Citrate	>99
Fluoride	95
Iodide	>99
Oxalate	98
Phosphate	95
Tartrate	97
Thiosulfate	99

[a]All anions were added in the form of sodium salts (1 mg/ml).

Se(IV) show no extraction. It is important to note that the extraction behavior of Hg(II) is different from these metal ions. Therefore, mercury(II) can easily be separated from these elements, and their separation factors are high enough for all practical applications. However, Tl(I), Co(II), Fe(III), and Pt(IV) show partial extraction and can be eliminated in three to four scrub stages.

Selectivity of the extraction/separation of mercury was checked by carrying out the extractive separation of mercury from a synthetic mixture containing Cs(I), Ba(II), Cr(III), In(III), As(III), and Se(IV) (7.5 mg each) labeled with their gamma-emitting radiotracers and ^{203}Hg in trace amounts. The mixture was equilibrated according to the procedure described, and the separated mercury was found to be more than 99% pure by gamma spectrometry. However, the separation factors of a few elements which do not appear high can be improved significantly in two or three scrub stages, which will not affect the recovery of mercury because of its high *D* values while it does eliminate impurities from the organic phase.

A study was carried out to determine whether large aqueous to organic phase ratios could efficiently extract the metal. It was found that with aqueous to organic volume ratios up to 100: 1, mercury can be extracted at >95% efficiency with a 0.1 *M* DPPM-benzene solution. Mercury interferes in the determination of selenium (*9*) and indium (*10*) by atomic absorption spectrometry. This separation procedure, therefore, can be utilized to remove traces of mercury from the matrix before the measure-

TABLE 2

Distribution Coefficients and Separation Factors of Different Elements with Respect to Hg(II) from 1 *M* HCl Containing 0.02 *M* KSCN by 0.1 *M* DPPM in Benzene

Metal[a] ion	Concentration (*M*)	Distribution coefficient	Separation factor
Na(I)	10^{-4}	0.00	$>10^5$
K(I)	10^{-4}	0.00	$>10^5$
Cs(I)	10^{-6}	0.00	$>10^5$
Tl(I)	10^{-5}	0.33	$>10^2$
Mn(II)	10^{-5}	0.00	$>10^4$
Co(II)	10^{-6}	0.55	$>10^2$
Ni(II)	10^{-5}	0.02	$>10^3$
Cu(II)	10^{-5}	1.12	$\sim10^3$
Zn(II)	10^{-4}	66.0	2.2
Sr(II)	10^{-6}	0.00	$>10^4$
Cd(II)	10^{-6}	0.12	$\sim10^3$
Ba(II)	10^{-6}	0.00	$>10^4$
Hg(II)	10^{-6}	147	—
Sc(III)	10^{-5}	0.00	$>10^4$
Cr(III)	10^{-5}	0.00	$>10^4$
Fe(III)	10^{-4}	0.32	$>10^2$
As(III)	10^{-4}	0.00	$>10^4$
In(III)	10^{-5}	0.01	$\sim10^4$
Eu(III)	10^{-6}	0.00	$\sim10^5$
Se(IV)	10^{-6}	0.01	$>10^3$
Hf(IV)	10^{-4}	0.01	$\sim10^4$
Pt(IV)	10^{-4}	0.46	$>10^2$
Pb(IV)	10^{-5}	2.66	55.2
Sb(V)	10^{-5}	0.04	$>10^3$

[a]Added as chloride.

ment of the two elements. Moreover, mercury can be preconcentrated by employing this extraction procedure before its atomic absorption measurement is made in order to reduce matrix and interference effects and to increase the sensitivity (*11*). In addition, in the neutron activation analysis of mercury and zinc, selenium and scandium cause interferences, respectively (*12*), and it is evident from Table 2 that mercury and zinc can easily be separated from selenium and scandium. Therefore, these interferences can be removed by applying this extraction method prior to the determination of mercury and zinc.

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