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Extraction Behavior of Zinc(II), Cadmium(II), Mercury(II), Indium(III), and Thallium(III) as Thiocyanates in High-Molecular-Weight Amines and Some Mutual Binary Separations

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NOTE

Extraction Behavior of Zinc(II), Cadmium(II), Mercury(II), Indium(III), and Thallium(III) as Thiocyanates in High-Molecular-Weight Amines and Some Mutual Binary Separations

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Abstract

The extraction behavior of Zn(II), Cd(II), Hg(II), In(III), and Tl(III) has been studied at different NH_4CNS molarities in some commercially available liquid anion exchangers. The effect of such variables as the type of amine, molarity of NH_4CNS, and pH of aqueous phase and organic diluent on extraction has been explored to achieve the best conditions of some mutual binary separations of analytical and radiochemical interest.

INTRODUCTION

High-molecular-weight amines, popularly known as liquid anion exchangers, uniquely combine some of the advantages of liquid–liquid extraction and ion-exchange. In the last two decades a large number of papers has been published (*1*, *2*) on the extraction of anionic metal complexes in various high-molecular-weight amines, and the data have been utilized for the separation of different metals. Practically insignificant attention has been paid to the extraction of metals in liquid anion exchangers from aqueous thiocyanate media. Moore (*3*) used the Aliquat 336–thiocyanate system for the separation of some lanthanides and actinides. It was considered important to study the extraction behavior of Zn(II), Cd(II), Hg(II), In(III), and Tl(III) as thiocyanates in some of the

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commercially available liquid anion exchangers and use the data for obtaining mutual binary separations. The extraction behavior of this group of elements is fairly interesting to study as many of their mutual separations will be of analytical and radiochemical importance. The separations involving cadmium and mercury will be of interest to environmentalists because these two elements are serious pollutants of the biosphere.

The present communication reports the behavior of Zn(II), Cd(II), Hg(II), In(III), and Tl(III) in various high-molecular-weight amines at different thiocyanate molarities. The effect of the pH of the aqueous phase and the organic diluent on extraction has also been investigated. Based on the data, some mutual binary separations of these elements with high separation factors are reported. The advantage of the amine–thiocyanate system for some of the separations reported herein is also discussed.

EXPERIMENTAL

Materials

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In the present study, Primene JM-T, Amberlite LA-1, Alamine 336, and Aliquat 336 were used as the representatives of primary, secondary, tertiary amines, and quaternary ammonium salt, respectively. Aliquat 336 was converted into its thiocyanate salt by equilibrating its solution with 2 *M* ammonium thiocyanate solution. These liquid anion exchangers were practical grade materials. ^{65}Zn, ^{115m}Cd, ^{203}Hg, ^{114m}In, and ^{204}Tl radioisotopes supplied by Bhabha Atomic Research Centre, Bombay, India were used as tracers. All other reagents used were of analytical purity.

Procedure

The amine solution was made up 0.1 *M* in chloroform or benzene. The metal ion solution (1.0×10^{-4} *M*) consisted of metal sulfate or nitrate in ammonium thiocyanate solution of appropriate concentration. A small countable amount of ^{65}Zn, ^{115m}Cd, ^{203}Hg, ^{114m}In, and ^{204}Tl activity was added to each of the respective metal solution. Equal volumes of organic amine solution and aqueous metal–thiocyanate solution were mixed together in a separatory funnel and shaken on a mechanical shaker for about 5 min to ensure complete equilibration of the two phases. After clear separation of the two phases, equal aliquots of each phase were removed for counting. Gamma counting of ^{65}Zn, ^{203}Hg, and ^{114m}In was done on a NaI(Tl) well-type scintillation counter. In the case of ^{115m}Cd and ^{204}Tl, beta counting was done using a G.M. counter. The distribution ratio, percent extraction, and separation factor were calculated by the usual methods. In the case of gamma counting the values of percent extraction showed a precision of approximately ±1% at 55% extraction while it was about ±2% for beta counting. Each experiment was run in duplicate and the average values are reported. The effect of metal ion concentration on the distribution ratio was found to be insignificant. All the distribution studies were done at room temperature (20 ± 3°C).

Before carrying out thiocyanate extractions the blanks due to the extraction of the metals as sulfate or nitrate in various amines were checked and found to be negligible. Moreover, it was found that the sulfate or nitrate ions present at the concentration of the aqueous phase do not interfere in the extractions.

RESULTS AND DISCUSSION

The effect of pH of the aqueous phase on the extraction of metals as thiocyanate was studied in the Alamine 336–benzene system at 1.0 *M* thiocyanate concentration and was found to be negligible (±2%) within the pH range 2.0 to 5.0. The dependence of extraction of various metals in different amines on the molarity of ammonium thiocyanate is shown in Figs. 1–3. The pH of 0.1 to 4.0 *M* aqueous NH_4CNS solution lies between 2 and 4, hence any effect due to hydrogen ion concentration is taken to be insignificant. The extractions of Zn(II), Cd(II), and Hg(II) in Primene JM-T, Amberlite LA-1, and Alamine 336 increase with decreasing thiocyanate molarity with a tendency to attain a limiting value. However, the extractions of these elements in Aliquat 336 are almost quantitative over the entire investigated thiocyanate molarity range. In the case of In(III), reproducible data are obtained only in Aliquat 336; therefore the results of extractions in other amines are not given. The extraction of In(III) in Aliquat 336 is quantitative over the entire thiocyanate molarity range. Tl(III) shows negligible extraction (<2%) in all the amines over the investigated thiocyanate concentration range. The behavior of In(III) and Tl(III) is not shown in the figures.

The extraction behavior of all these elements is more or less similar to their sorption on solid anion exchange resins (*4–6*). For the extraction of Zn(II), Cd(II), and Hg(II), the extraction efficiency of various amines follows the expected order: primary < secondary $\lesssim$ tertiary < quaternary. The extractions of these elements in a particular amine are in ac-

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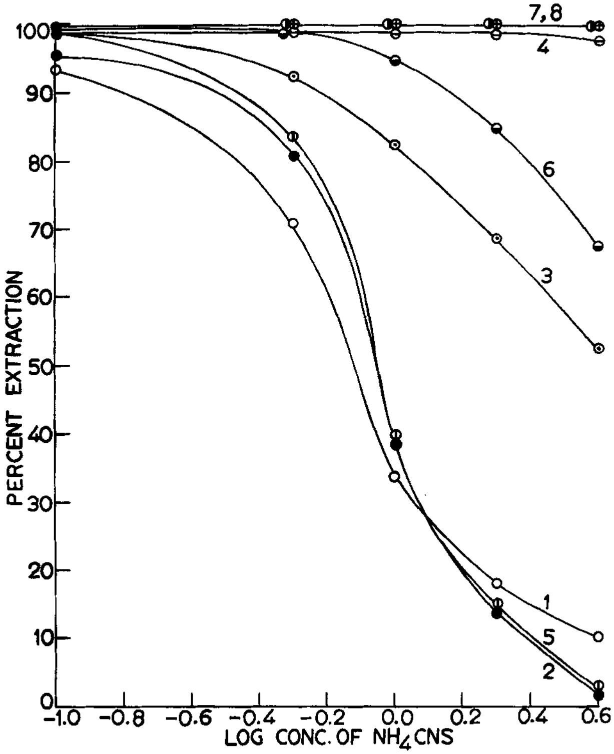

FIG. 1. Extraction of Zn(II) from NH_4CNS solutions by various 0.1 *M* amines in chloroform and benzene. Chloroform solvent: (1) Primene JM-T, (2) Amberlite LA-1, (3) Alamine 336, (4) Aliquat 336. Benzene solvent: (5) Primene JM-T, (6) Amberlite LA-1, (7) Alamine 336, (8) Aliquat 336.

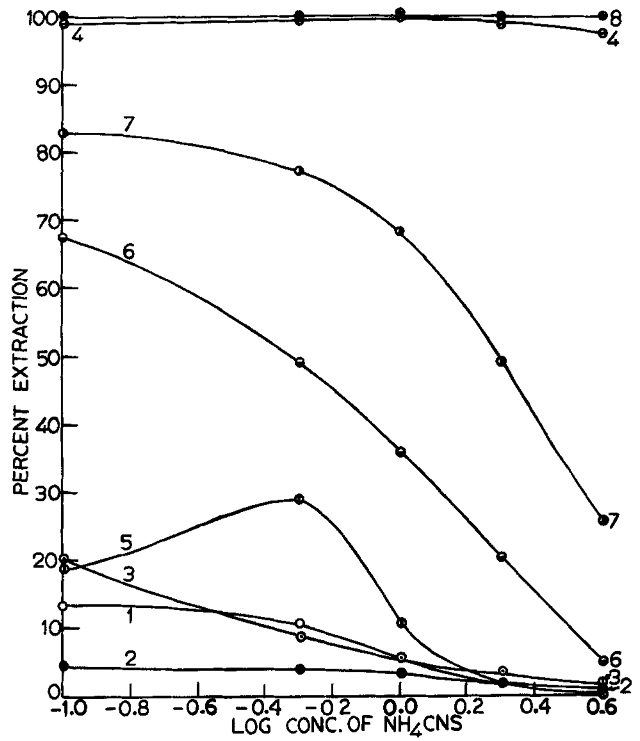

FIG. 2. Extraction of Cd(II) from NH_4CNS solutions by various 0.1 *M* amines in chloroform and benzene. Chloroform and benzene solvents keyed as in Fig. 1.

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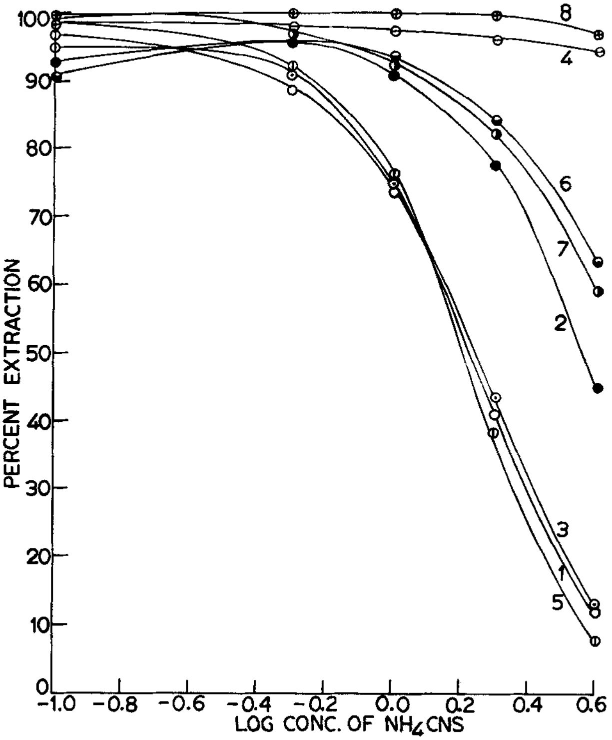

FIG. 3. Extraction of Hg(II) from NH_4CNS solutions by various 0.1 *M* amines in chloroform and benzene. Chloroform and benzene solvents keyed as in Fig. 1.

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TABLE 1

Some Binary Separations of Zn(II), Cd(II), Hg(II), In(III), and Tl(III) in 0.1 *M* Amines

Metals separated	Extractant	Molarity of NH_4CNS	Separation factor
Zn(II) from Cd(II)	Amberlite LA-1 in chloroform	0.1	361
	Alamine 336 in chloroform	0.5	130
Hg(II) from Cd(II)	Amberlite LA-1 in chloroform	0.5	456
	Alamine 336 in chloroform	0.5	281
Zn(II) from Tl(III)	Aliquat 336 in benzene	0.1–4.0	$>10^5$
	Aliquat 336 in chloroform	0.1–4.0	$>10^4$
Hg(II) from Tl(III)	Aliquat 336 in benzene	0.1–4.0	$>10^4$
	Aliquat 336 in chloroform	0.1–4.0	$>10^4$
Cd(II) from Tl(III)	Aliquat 336 in benzene	0.1–4.0	$>10^5$
	Aliquat 336 in chloroform	0.1–4.0	$>10^4$
In(III) from Tl(III)	Aliquat 336 in benzene	0.1–4.0	$>10^5$
	Aliquat 336 in chloroform	0.1–4.0	$>10^5$

cordance with the stability of their respective thiocyanate complexes, i.e., Hg > Zn > Cd. This effect could not be discerned in Aliquat 336 because of quantitative extractions of all the three elements in it. From the figures it is apparent that generally the extractions are higher with benzene as diluent compared to those with chloroform as diluent.

This study offers various aqueous and organic amine conditions for the binary separations of some of these elements with high separation factors. The separation of zinc from cadmium can be obtained in chloroform solution of Amberlite LA-1 at 0.1 *M* NH_4CNS. Under these conditions around 95% zinc is extracted in the organic layer, leaving behind about the same amount of cadmium in the aqueous phase. Zn(II) can be quantitatively stripped from the organic layer with 0.1 *M* nitric acid. The same separation is also achieved in a chloroform solution of Alamine 336 at

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0.5 *M* NH_4CNS. Cd(II) can be separated from Hg(II) in a chloroform solution of Amberlite LA-1 at 0.5 *M* NH_4CNS when almost all the mercury is extracted in the organic phase with less than 5% cadmium with it. The same separation can also be obtained by extracting Hg(II) in a chloroform solution of Alamine 336 at 0.5 *M* NH_4CNS. Almost quantitative recovery of mercury from the organic layer can be obtained by washing it with 4 *M* HNO_3. Zn(II), Cd(II), Hg(II), and In(III) can be quantitatively separated from Tl(III) in both benzene and chloroform solutions of Aliquat 336 at any molarity of NH_4CNS ranging from 0.1 to 4.0 *M*. In all these cases Zn(II), Cd(II), Hg(II), and In(III) can be quantitatively recovered from the organic layer by washing it with 4 *M* HNO_3. The conditions of the above separations, along with the separation factors, are listed in Table 1.

The amine–thiocyanate system offers some definite advantage over the use of anion-exchange resins for obtaining the above-mentioned separations from aqueous thiocyanate media. On anion-exchange resins, Cd(II) cannot be easily separated from Zn(II), and Hg(II) from thiocyanate solutions, while these separations are attained with good separation factors by extraction in amine solutions. The separation of Zn(II), Cd(II), Hg(II), and In(III) from Tl(III) can be obtained on solid resins with comparable separation factors, but the rapidity of the extraction procedure scores over column separations.

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REFERENCES

1. H. Green, *Talanta*, *11*, 1561 (1964).
2. H. Green, *Ibid.*, *20*, 139 (1973).
3. F. L. Moore, *Anal. Chem.*, *36*, 2158 (1964).
4. A. K. Majumdar and B. K. Mitra, *Z. Anal. Chem.*, *208*, 1 (1965).
5. G. Alexandrides and C. J. Cumminskey, *J. Inorg. Nucl. Chem.*, *28*, 2055 (1966).
6. J. F. Neumann, J. R. Paxson, and C. J. Cumminskey, *Ibid.*, *30*, 2243 (1968).

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