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METAL ION SEPARATIONS IN THIOCYANATE MEDIA USING A LIQUID ANION EXCHANGER*

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SUMMARY

The liquid ion exchanger investigated, Alamine 336, may be used to effect numerous separations of metal ions in thiocyanate media. Some separations have been quantitatively demonstrated while others are suggested by the analogous behavior of metal ions in their particular extraction group. Under the mild conditions used in this study, *i.e.* room temperature and pressure, 10–30% (v/v) solution of exchanger in toluene, thiocyanate and acid concentrations less than 1.0 *M*, the physical handling of the amine was no problem. Phase separations were quick and clean for the solvent extraction work and there was no problem of extractant bleeding from the support in the reversed-phase column work.

INTRODUCTION

The use of liquid ion exchangers for the extraction of metal ions from thiocyanate media has been reported previously. MOORE[1] investigated the extraction of yttrium(III) from 7–8 *M* thiocyanate solutions into a xylene solution of methyldioctylamine (MDOA). SHEPPARD[2] examined the extraction behavior of americium, curium, berkelium, californium and einsteinium between aqueous 5 *M* ammonium thiocyanate and a xylene solution of tri-*n*-octylamine (TOA). HUFF[3] applied the liquid extraction data of MOORE[4] and GERONTOPULOS *et al.*[5] to column partition chromatographic studies of americium, yttrium and rare earths using Aliquat 336 as the sorbed liquid and aqueous eluents of 0.1 *M* to 0.4 *M* ammonium thiocyanate.

Several papers concerned with the extraction of cobalt from thiocyanate solution utilized Aliquat 336 in benzene[6] and triisooctylamine (TIOA) in carbon tetrachloride[7] for the spectrophotometric determination of cobalt(II) in the colored organic phase. WATANABE AND AKATSUKA[8] used TOA dissolved in various diluents to study the extraction of cobalt(II) from aqueous thiocyanate solutions.

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BRINKMAN *et al.*[9] used five different liquid ion exchangers impregnated on paper and thin-layer adsorbents to study the behavior of copper(II), cadmium(II), lead(II), cobalt(II), manganese(II) and silver(I) in 0–10 *M* thiocyanate solutions. PRZESZLAKOWSKI[10] used paper chromatography to study the extraction of a large number of metal ions between aqueous ammonium thiocyanate–hydrochloric acid mixtures and TOA, TIOA and tri-*n*-butylamine.

The purpose of this work is to investigate the analytical potential of a weak base liquid ion exchanger, Alamine 336, for the solvent extraction and reversed-phase column chromatographic separation of metal ions in thiocyanate media. Much of the quantitative work in the literature has been directed toward the lanthanide and actinide metals using fairly concentrated thiocyanate solutions. Thiocyanic acid is a strong acid and thiocyanate ion forms complexes with numerous metal ions[11,12], so it should be possible to perform separations with Alamine 336 using mild conditions, *i.e.* dilute solutions of thiocyanate (<1.0 *M*) and acid (~ 0.5 *M*).

APPARATUS AND CHEMICALS

A Perkin-Elmer Model 290 atomic absorption spectrophotometer equipped with a Perkin-Elmer combination cobalt, chromium, copper, manganese and nickel hollow cathode lamp was used for the atomic absorption analysis of cobalt, copper and nickel. An air–acetylene flame was used throughout.

Commercial Alamine 336 (tricapryl tertiary amine) was obtained from General Mills, Inc., and used without further purification. The company gives a typical analysis as showing 95% tertiary amine content, 1% secondary amine content, 0.2% primary amine content and 0.0% water.

The column support, Chromosorb W (non-acid washed, 80–100 mesh), was obtained from Johns-Manville Products Corporation and was washed successively with 6 *M* hydrochloric acid, distilled water, acetone and oven dried at 110° before use.

The reagent grade chloride, nitrate or oxide salt of the metal was diluted to a final acid concentration of 0.5 *M* unless hydrolysis was a problem. Gallium and indium solutions were prepared from the 99.99% pure metal. Synthetic sample mixtures for column separation studies were prepared by mixing given volumes of standardized metal ion solution and eluent (acidic solutions of potassium thiocyanate were prepared immediately before use). The sample volume added to the column was either 1 or 2 ml.

EXPERIMENTAL

Alamine 336 (R_3N) was diluted with toluene and converted to the thiocyanate form ($R_3NH^+SCN^-$) by equilibrating three times with an equal volume of a solution 1.0 *M* in potassium thiocyanate and 0.5 *M* in hydrochloric acid followed by a water wash. A 20% (v/v) solution of R_3N in toluene is 0.4 *M* (ref. 13).

Solvent extraction batch distribution ratios were determined by equilibrating equal volumes of organic and aqueous phases. Aliquots of the aqueous phase were taken and the metal ion concentration determined using an appropriate analytical method. The amount of metal ion in the organic phase was determined by material balance.

The reversed-phase column chromatographic columns were prepared by dissolving x ml of Alamine 336 in ether and then continuously slurrying with y g of support in an open vessel until no ether fumes were present (the maximum load is approximately 20 ml/17.5 g). The dry coated support was slurried in a solution 1.0 M in potassium thiocyanate and 0.5 M in hydrochloric acid, then poured into a column and allowed to settle via gravity flow.

Conditions for determination of copper(II), cobalt(II) and nickel(II) by atomic absorption are those recommended by the Perkin-Elmer Co.

RESULTS AND DISCUSSION

Distribution data were determined for 29 metal ions between an aqueous phase of 0.063 M KSCN–0.5 M HCl and an organic phase of 20% (v/v) $R_3NH^+SCN^-$ in toluene. A 5-min equilibration period was used mainly for convenience because a series of gallium(III) extractions performed using initial aqueous solutions of 0.5 M HCl, 0.30 M KSCN–0.5 M HCl and 0.70 M KSCN–0.5 M HCl indicated that equilibrium was attained within 60 sec.

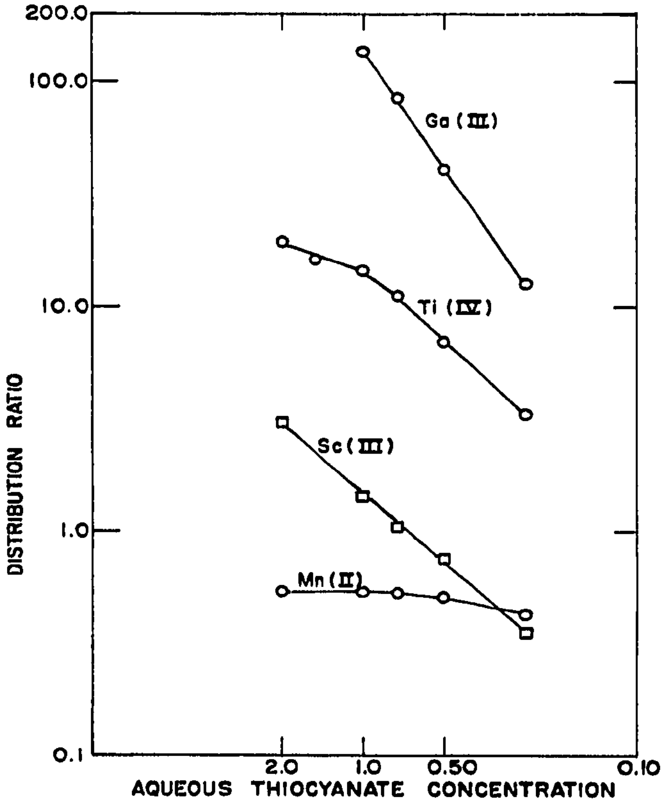

Fig. 1. Distribution ratio as a function of thiocyanate concentration.

The volume distribution ratio, D_v, was calculated as follows:

$$D_v = \frac{\text{total concentration of metal ion in organic phase}}{\text{total concentration of metal ion in aqueous phase}}$$

The extraction data indicate that the metal ions studied may be divided into three distinct groups:

Group 1—Low extraction, $D_v < 0.10$. Ions included are Al(III), Ba(II), Ca(II), Eu(III), La(III), Lu(III), Mg(II), Ni(II), Pb(II), Sr(II), Th(IV), Y(III).

Group 2—High extraction, $D_v > 30.0$. Ions included are Bi(III), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), In(III), Pd(II), Sn(IV), U(VI), Zn(II), Mo(VI).

Group 3—Intermediate extraction, $D_v = 0.2$–2.0. Ions included are Ga(III), Hf(IV), Mn(II), Sc(III), Ti(IV), Zr(IV).

The effect of increasing aqueous thiocyanate concentration on the distribution ratios of four intermediate extraction group ions is shown in Fig. 1. Two ions from the low percentage extraction group, thorium(IV) and nickel(II), were included in this study of increasing thiocyanate concentration. Their behavior is quite different from the intermediate extraction group ions, with the exception of manganese(II), because their extraction does not increase significantly over the entire thiocyanate concentration range studied. At 1.0 *M* thiocyanate the distribution ratios for nickel and thorium are still less than 0.03. Thus the possibility exists for column separations involving an ion or ions from each extraction group simply by controlling the thiocyanate concentration of the eluent.

Separations

The magnitude of the distribution data suggests that it should be possible to extract any combination of ions in Group 2 from any combination of ions in Group 1. Two practical applications of this concept were the removal of interfering metal ions from water prior to the determination of hardness via the method of FRITZ *et al.*[14], and the quantitative separation of cobalt and nickel.

Water hardness

Traces of dissolved iron, copper, cobalt and certain other metal ions may

TABLE I

REMOVAL OF Fe(III), Cu(II) AND Co(II) FROM HARD WATER SAMPLES
Column: 1.0 cm × 6.0 cm of Alamine 336 impregnated Chromosorb W.

No.	*Sample*	*Flow rate*	*Titration results*	
			Initial hardness (p.p.m.)	*Hardness found (p.p.m.)*
1	20 p.p.m. Fe(III), 20 p.p.m. Cu(II) and 10 p.p.m. Co(II) as $CaCo_3$	80 ml at 4 ml/min 150 ml at 12 ml/min	93.0	93.0
2	Same as 1	100 ml at 9 ml/min	93.0	91.8
3	20 p.p.m. Cu(II), 20 p.p.m. Fe(III) and 2 p.p.m. Co(II) as $CaCO_3$	400 ml at 9 ml/min	110.3	109.9[a] 109.9[b] 109.9[c]

[a] First 150 ml.
[b] Second 150 ml.
[c] 300–400 ml fraction.

interfere with water hardness titrations by reducing the sharpness of the end point or completely preventing a color change. Cyanide masks these metals if their concentration is not too great, but its use is hazardous.

The solvent extraction separation procedure involved extraction of 200 ml of hard water, containing 50 p.p.m. each of Fe(III), Co(II), and Cu(II) as $CaCO_3$, with 200 ml of 20% (v/v) exchanger and then 20 ml of a 20% (v/v) solution of Alamine 336 in toluene. Titrations of aliquots of the aqueous phase indicated an average hardness of 111.7 p.p.m., which corresponds favorably to the initial hardness of 110.3 p.p.m.

This separation problem was also attempted using a column procedure which would be more suitable for handling large volumes of water on a continuous basis. Table I lists the conditions and results of three such separations. In all cases the indicator change at the equivalence point was excellent and a comparison of total initial hardness and total hardness found indicates within experimental error no calcium or magnesium was lost during extraction. These separations are fast and the conditions used are mild. The water sample is not pretreated in any manner except to adjust the pH below 1.0 for the solvent extraction procedure.

Preparation of cobalt-free nickel salts

The very favorable separation factor between Group I and Group 2 metal ions, plus the fact that metal ions may be extracted from acidic aqueous solutions without direct addition of a complexing agent to the aqueous phase, makes Alamine 336–thiocyanate potentially useful for larger-scale separations such as the purification of metal salts. Although many possibilities exist the removal of small amounts of cobalt(II) from nickel(II) salts was selected for further study. Batch extraction

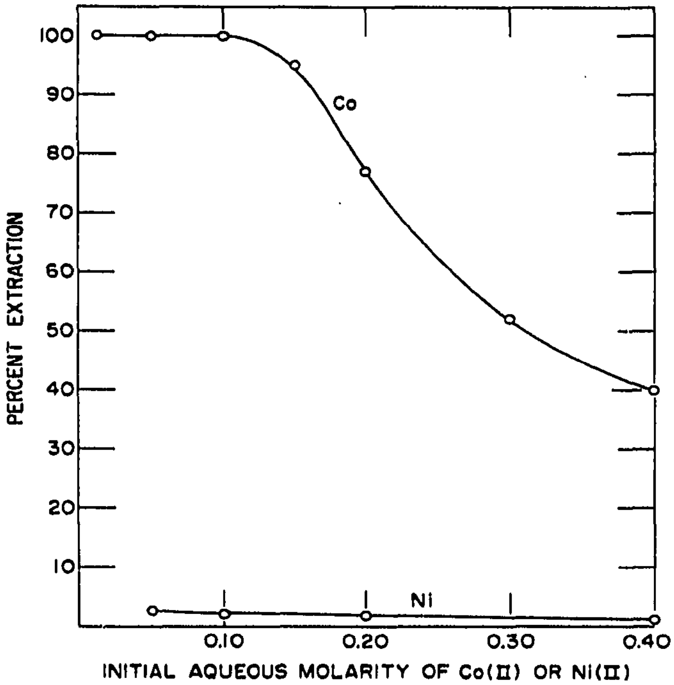

Fig. 2. Percent extraction of Co(II) or Ni(II) from 0.1 M HNO_3 into an equal volume of 0.6 M $R_3NH^+SCN^-$ in toluene (*i.e.* 9 mmoles).

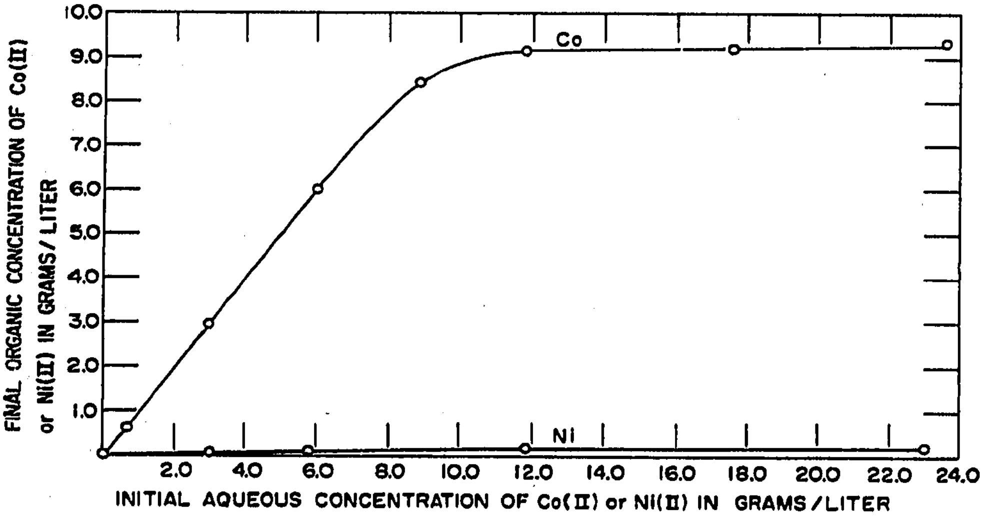

Fig. 3. Loading study for the extraction of Co(II) or Ni(II) from 0.1 M NHO$_3$ into an equal volume of 0.6 M $R_3NH^+SCN^-$ in toluene (*i.e.* 9.0 mmoles).

with $R_3NH^+SCN^-$ in toluene was used, although the use of a reversed-phase chromatographic column might be advantageous in some instances.

Figs. 2–4 show the results of a loading study performed by extracting increasing concentrations of cobalt(II) and nickel(II) individually with no thiocyanate initially present in the aqueous phase. Two extractions were also performed on nickel–cobalt mixtures with concentration ratios of 0.27 M/0.055 M and 0.27 M/0.027 M. The

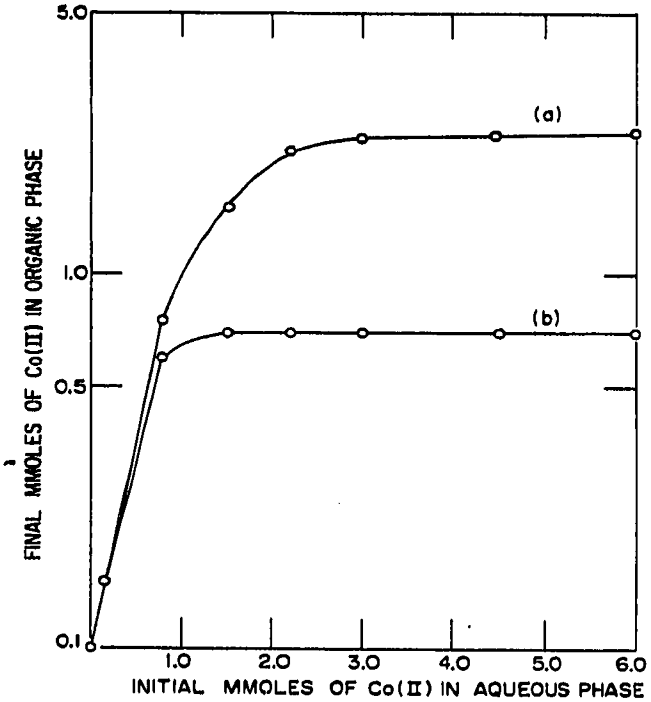

Fig. 4. Limiting loading curve for the extraction of Co(II) from 0.1 M nitric acid into (a) 9.0 mmoles of 30% (v/v) solution of $R_3NH^+SCN^-$ in toluene and (b) 3.0 mmoles of 10% (v/v) solution of $R_3NH^+SCN^-$ in toluene.

cobalt extraction was still complete while the nickel extraction actually decreased.

Fig. 2 indicates that a small amount of nickel is extracted for conditions under which cobalt is 100% extracted. Essentially all of this nickel may be recovered (cobalt-free) with two washings of dilute acid. Although there is no thiocyanate originally present in the aqueous phase, some partitioning occurs when equilibrium is attained between the organic and aqueous phases. The matrix element solution now contains thiocyanate ion, which may be undesirable. This is a minor problem because the aqueous thiocyanate can be removed by anion exchange or destroyed by boiling with nitric acid. When the organic phase becomes heavily loaded, the cobalt may be back-extracted with two washings of 1-*M* sulfuric acid, which converts much of the exchanger to the sulfate form, necessitating a reconversion before use.

Using Fig. 4 the cobalt to amine ratio for the extraction may be determined by the limiting loading method[15]. For the 30% solution the limiting cobalt/amine ratio is 2.34/9.0 = 1/3.85. For the 10% solution the limiting cobalt/amine ratio = 0.70/3.0 = 1/4.28. These results indicate a cobalt/amine ratio of 1/4. However, only one half the exchanger capacity was utilized because there was no thiocyanate initially present in the aqueous phase. Therefore, the equation for extraction may be written as:

$$4R_3NH^+SCN^- + Co(NO_3)_2 \rightleftharpoons (R_3NH^+)_2Co(SCN)_4^{2-} + 2R_3NH^+NO_3^-$$

Column separations

A series of nickel–copper and nickel–cobalt separations were achieved for concentration ratios ranging from 1/100 to 1000/1. These separations were performed to illustrate further the speed and ease with which ions from Groups 1 and 2 may be separated. The column was only 1.0 cm × 9.0 cm and the nickel was washed through at a flow rate of 1.0 ml/min with 25 ml of 0.1 *M* HNO_3 while the cobalt or copper was stripped with 25 ml of methanol at a flow rate of ∼3–5 ml/min.

Separations of this type can be very advantageous for the isolation of trace constituents from matrix elements which interfere with the analysis of the minor component. A pragmatic example of this concept occurred in the atomic absorption analysis of nickel in NBS standard sample 124d. This sample consists of the following elements and percentage composition:

Cu—83.60%
Pb—5.20%
Zn—5.06%
Sn—4.56%
Ni—0.99%
Fe—0.18%
Sb—0.17%
Ag—0.02%
P—0.02%
As—0.02%
S—0.093%

A direct analysis of the sample resulted in only a 91.0% recovery of nickel. The error was traced to the presence of copper, which decreases the absorbance of nickel if present in concentration ratios greater than 5/1. The ratio for this sample was 83.6/0.99 = 84/1. After the copper (as well as Zn, Sn and Fe) was removed by passing the sample through a 2.0 cm × 9.0 cm reversed-phase column of Alamine 336–thiocyanate, the analysis for nickel showed 99.9% recovery.

Methanol is used to strip the highly sorbed metal ions and the Alamine 336 from the column. The presence of the liquid ion exchanger can be tolerated in the atomic absorption analysis of metal ions. However, the effect of the amine on the

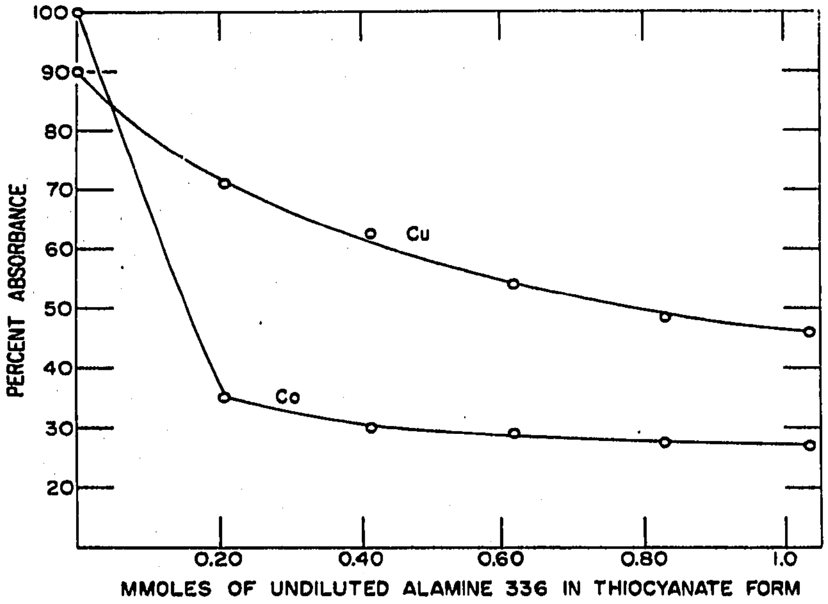

Fig. 5. Effect of $R_3NH^+SCN^-$ concentration on the atomic absorption determination of a methanolic 20 p.p.m. Co(II) solution or 20 p.p.m. Cu(II) solution. An air–acetylene flame was used.

absorbance of the metal ion should be investigated. It was found here and in cases cited by HARTLAGE[16] that certain amines will decrease the absorbance of metal ions. Fig. 5 shows the effect of $R_3NH^+SCN^-$ on the absorbance of methanolic solutions of copper and cobalt. HARTLAGE has shown that the interference may be overcome by using a nitrous oxide–acetylene flame, but there was also a decrease in sensitivity. The amine was no problem here because its concentration was always sufficient for the analysis to be performed on the flat portion of the curve (Fig. 5). The average recovery for fourteen Cu determinations by the non-aqueous atomic absorption method was 99.9 ± 2.28% and the average recovery for six Co determinations was 100.9 ± 3.02%.

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