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## THE USE OF AQUEOUS THIOCYANATE SOLUTIONS IN LIQUID-LIQUID EXTRACTION AND REVERSED-PHASE EXTRACTION CHROMATOGRAPHY. I

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### SUMMARY

Ten ions have been chromatographed on thin layers of cellulose impregnated with Aliquat 336, Alamine 336 S, Amberlite LA-1 or Primene JM-T, and on non-impregnated cellulose. Solutions of 0.3–7 M thiocyanate acidified with 0.01–1.0 N hydrochloric acid are used as eluents.  $R_F$  spectra and a number of separations are reported. Percentage extraction *versus*  $\text{NCS}^-$  molarity data and results of maximum-loading and spectroscopic measurements for the systems liquid anion exchanger–Co(II)– $\text{NCS}^-$  and liquid anion exchanger–Ni(II)– $\text{NCS}^-$  are also reported.

The sorption strength/extraction efficiency of the exchangers increases in the order Primene < Amberlite < Alamine < Aliquat. Increasing the acidity of the aqueous phase generally decreases the sorption/extraction of the complex metal-thiocyanato anions to a considerable extent. Sorption proceeds through anion exchange for all ions investigated. The Co(II)-containing species extracted into the organic phase is  $(\text{R}_3\text{R}'\text{NH}^+)_2\text{Co}(\text{NCS})_4^{2-}$  (R, alkyl; R', alkyl or H). Nickel is present in the organic phase predominantly as  $\text{Ni}(\text{NCS})_6^{4-}$ ; however, depending upon the diluent used,  $\text{Ni}(\text{NCS})_4^{2-}$  may also be present.

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### INTRODUCTION

Extraction of metal-thiocyanato complexes from aqueous solutions into water-immiscible solvents has been known for over 100 years. In 1863, Braun<sup>1</sup> showed that the coloured thiocyanato complex of molybdenum, which is formed upon reduction (however, see ref. 2) of molybdic acid with zinc in the presence of thiocyanate salts, is extracted by diethyl ether. Since that data, over 400 papers on thiocyanate extraction have been published, as can be ascertained from a recent literature review by Sultanova *et al.*<sup>3</sup>. Still, as these authors state, relatively little progress has been made in the elucidation of the mechanism(s) involved in thiocyanate extraction systems. Actually, results are rather meagre even as regards the extraction behaviour of HNCS itself. In recent years, high-molecular-weight amines and substituted quaternary ammonium salts, so-called liquid anion-exchangers, have shown high potential for use in liquid-liquid extraction and reversed-phase chromatography. However, here too, thiocyanate systems have been little exploited, despite promising

features such as the fact that metal–thiocyanato complexes are often more completely extracted than are, for example, metal–chloro complexes. In this paper, preliminary results of a systematic investigation of the liquid anion exchanger–NCS<sup>-</sup> system are reported.

## MATERIALS AND METHODS

Data on the anion exchangers used in the present study are given in Table I.

TABLE I  
CHARACTERISTICS OF SOME LIQUID ANION EXCHANGERS

Type	Name	Composition	Mean mol. wt.	Manufacturer
Primary	Primene JM-T	Trialkylmethylamine	310	Rohm and Haas*
Secondary	Amberlite LA-1	Dodecenylntrialkylmethylamine	372	Rohm and Haas*
Tertiary	Alamine 336 S	Tri- <i>n</i> -(octyl + decyl)amine	392	General Mills**
Quaternary	Aliquat 336	Methyltri- <i>n</i> -(octyl + decyl)-ammonium chloride	475	General Mills**

\* Philadelphia, Pa., U.S.A.

\*\* Kankakee, Ill., U.S.A.

### Chromatography

Chromatography was carried out as described in previous papers, using microcrystalline cellulose (Avicel TG104, Macherey, Nagel & Co., Düren, G.F.R.) as support. Amines are converted into their thiocyanate salts by equilibrating a 0.1 *M* solution in chloroform with an aqueous 2 *M* ammonium thiocyanate solution containing 0.12 *N* hydrochloric acid. Quaternary ammonium chlorides are converted into the corresponding thiocyanates by three consecutive equilibrations with 2 *M* ammonium thiocyanate solution containing 0.02 *N* hydrochloric acid. Suspensions of impregnated cellulose are prepared by thoroughly mixing the solution in cellulose–chloroform (1:4, w/v). The suspension is stored overnight and agitated again before use. Chromatoplates are prepared by dipping ordinary microscope slides into the suspension. After evaporation of the chloroform, a thin film of impregnated support material adheres to the slides; superfluous material is wiped off the back. Subsequently, a series of scores is made in the thin layer; as a result, six *ca.* 3.5-mm wide tracks appear on the chromatoplate, and small margins remain along the edges. Six spots (diameter *ca.* 1 mm) are applied on to each plate using a pointed paper wick partly impregnated with the solution to be analyzed. Sample solutions of the ions (as their chloride or nitrate salts) contain 1–10 mg/ml of cation. Ascending chromatography is carried out for a 3-cm run in suitable vessels, *e.g.*, Hellendahl staining jars. The development is terminated when the eluent reaches a previously applied groove in the cellulose layer. After drying the plates in the air, detection of all ions except Ag(I) and Cr(III) is achieved using a 0.2% solution of 4-(2-pyridylazo)resorcinol (PAR) in 80% ethanol, and subsequent treatment with ammonia vapour. Ag(I) is identified by spraying with a freshly prepared 0.2% solution of dithizone in 80% acetone, followed by treatment with ammonia. The spots of Cr(III) are made visible by spraying with

a 0.2% solution of diphenylcarbazone in 80% ethanol and subsequent heating to 200°. Details of the experimental procedure and the apparatus required are reported elsewhere<sup>4</sup>.

### Extraction

An aqueous Co(II) or Ni(II) solution of suitable composition is shaken for 20 min with an equal volume of a solution of a liquid anion exchanger (as its thiocyanate salt) in toluene. After separation of the phases, an aliquot of the organic phase is pipetted into an erlenmeyer flask and the metal ion content is determined titrimetrically using the extractive end-point determination described below (Co and Ni) or spectrophotometrically at  $\lambda = 630 \text{ nm}$  (Co only). UV-visible spectra are recorded on a Perkin-Elmer 402 spectrometer.

## RESULTS AND DISCUSSION

### Chromatography

In order to study the dependence of the extraction efficiency of the liquid anion exchangers on their structure, reversed-phase chromatography was performed for ten ions, viz., Al(III), Fe(III), Co(II), Ni(II), Zn(II), Ag(I), Cd(II), Pb(II), Th(IV) and U(VI). Solutions of 0.3–7 *M* ammonium thiocyanate acidified with 0.3 *N* hydrochloric acid were used as eluents. The results obtained with four exchangers, representing primary to tertiary amines and quaternary ammonium salts, are presented in Fig. 1. When using non-impregnated cellulose, all ions move with the solvent front over the whole NCS<sup>-</sup> concentration range investigated.

The results in Fig. 1 agree favourably with literature results obtained by reversed-phase paper (tertiary amines<sup>5</sup>) and thin-layer (secondary amine<sup>6</sup>) chromatography. They clearly demonstrate that the sorption strength of the exchangers in-

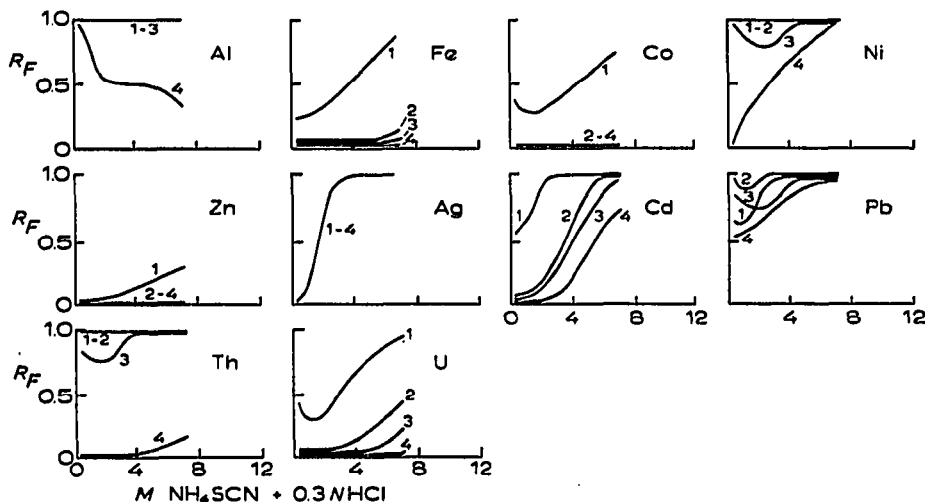


Fig. 1.  $R_F$  versus molarity of  $\text{NH}_4\text{NCS}$  spectra for ten ions, using cellulose impregnated with 1, Primene; 2, Amberlite LA-1; 3, Alamine 336 S; or 4, Aliquat 336.

creases in the order primary < secondary < tertiary < quaternary. This result contrasts with literature data on halide<sup>7</sup> and nitrate<sup>8</sup> systems. In these systems, sorption also increases from primary to tertiary exchangers; however, the behaviour of tertiary and quaternary exchangers usually does not differ significantly. In order to ascertain whether the divergent behaviour of tertiary and quaternary exchangers is a characteristic of thiocyanate systems, next to Aliquat and Alamine, three further pairs of structurally related tertiary and quaternary exchangers were studied. With Adogen 464 and 368 (mean mol.wt. 430; Archer-Daniels-Midland, Minneapolis, Minn., U.S.A.), which have a composition roughly comparable with that of Aliquat and Alamine, respectively, the sorption strength of the quaternary compound also surpasses that of its tertiary analogue. However, when using extractants with lower molecular weights, such as tri- and tetra-*n*-butyl- and tri- and tetra-*n*-hexylammonium thiocyanates, the differences in sorption strength between the two classes of exchangers disappear. No satisfactory explanation for these phenomena (experimental details of which will be published elsewhere<sup>9</sup>) can as yet be forwarded. However, in itself it is noteworthy that tri- and tetrabutylammonium salts can serve as useful impregnants in reversed-phase chromatography in thiocyanate systems; for it is known<sup>10</sup> that in chloride systems, for example, the butylammonium salts dissolve in the aqueous mobile phase and appear as a dark, oily band immediately behind the solvent front.

In order to study the influence of the acidity of the mobile phase on the  $R_F$  values of the metal ions, experiments were performed on Aliquat-impregnated cellulose, using solutions of ammonium thiocyanate containing 0.01–1.0 *N* hydrochloric acid as eluents. The  $R_F$  spectra in Fig. 2 indicate that increasing the acidity of the eluent decreases the sorption of all ions except Ag(I). No results are included for Fe(III), Co(II) and Zn(II), because these ions have  $R_F = 0.0$  in all instances. Their movement is negligibly small even when Aliquat is replaced with the much weaker sorbing Amberlite LA-1. Obviously, changing the acidity of the eluent is a powerful means of creating suitable conditions for metal ion separations.

As regards Ag(I), its  $R_F$  values at a fixed ammonium thiocyanate concentration vary neither with the type of exchanger selected for impregnation of the support nor with the acidity of the mobile phase. Usually, such behaviour indicates that the

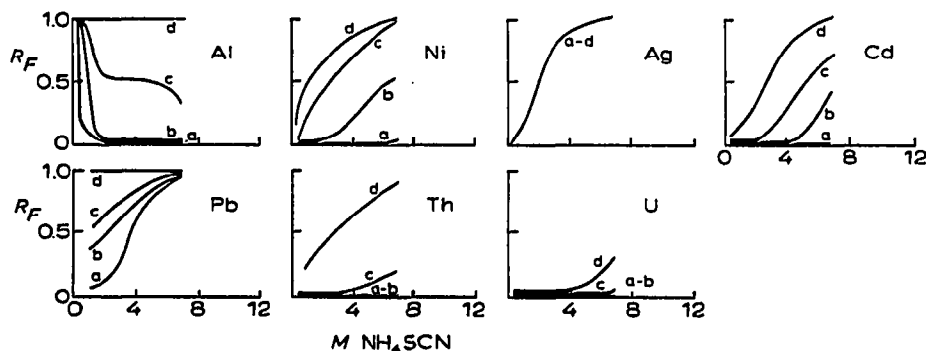
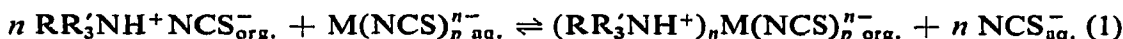


Fig. 2. Dependence of  $R_F$  values on acidity of the mobile phase. Stationary phase: cellulose impregnated with Aliquat 336. Mobile phase: solutions of  $\text{NH}_4\text{NCS}$  containing the following concentrations of HCl: a, 0.01 *N*; b, 0.1 *N*; c, 0.3 *N*; d, 1.0 *N*.

anion exchangers do not play a significant role, *i.e.*, phenomena such as adsorption to the support and precipitation of insoluble metal salts govern the sorption process. However, in the present case, Ag(I) moves with the solvent front on non-impregnated cellulose. Therefore, one must conclude that a specific interaction of the silver-thiocyanato complex ion with the liquid anion exchangers does occur.

The overall results indicate that for the ions under investigation, the sorption process may be represented by



(R, alkyl; R', alkyl or H).

It is interesting to note that in most instances the  $R_F$  values increase monotonously with increasing acid *and* thiocyanate concentration. This is in marked contrast with the results reported for exchanger-hydrochloric acid systems<sup>7</sup>, in which sorption often increases with increasing hydrochloric acid concentration. Obviously, strong complexation between metal ions and  $\text{NCS}^-$  often already occurs at low  $\text{NCS}^-$  concentrations. Desorption at higher concentrations may be attributed to factors such as the strong competition due to the uptake of HNCS in excess of the amount necessary for stoichiometric neutralization of the amine, *i.e.*, to the formation of  $\text{RR}'_3\text{NH}^+\text{NCS}^- \cdot x\text{HNCS}$ , increasing competition of the excess of  $\text{NCS}^-$  itself, and/or the formation of higher metal-thiocyanato complexes, which are expelled from the organic phase on account of their high negative charge.

Lastly, as regards eqn. 1, direct proof of the nature of the sorbed metal-thiocyanato complex was obtained in the case of Co(II). A spot of the metal ion, applied to cellulose impregnated with Aliquat<sup>+</sup> $\text{NCS}^-$  and eluted with an aqueous ammonium thiocyanate solution, was scanned over the range 270–750 nm using a Zeiss PMQ II spectrometer with a thin-layer attachment. The UV-visible absorption spectrum of the spot is virtually identical with that recorded for Co(II)-containing extracts obtained in liquid-liquid extraction: maxima occurring at 630, 592 (shoulder) and 333 nm demonstrate that the sorbed complex ion is  $\text{Co}(\text{NCS})_4^{2-}$  (see below).

*Separations.* Some examples of separations are shown in Fig. 3. Particular attention is drawn to the analysis of the mixture of Al(III), Cr(III) and Ni(II). For most chromatographic systems, the separation of these ions meets with considerable problems, owing to their weak complexing tendency with inorganic ligands. It is

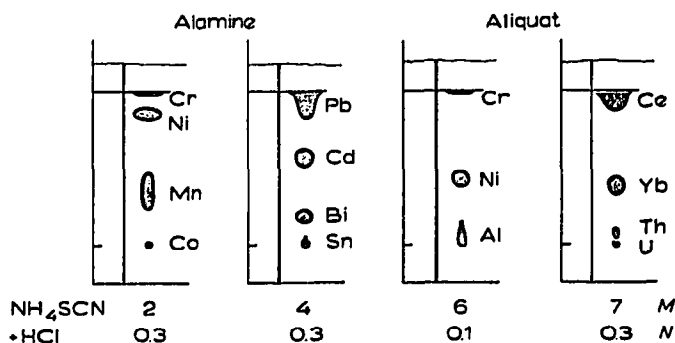


Fig. 3. Examples of thin-layer separations in two liquid anion exchanger- $\text{NH}_4\text{NCS}$  systems.

interesting to note that in the present system, Cr(III), the very ion known to form a series of well defined anionic thiocyanato complexes, moves with the solvent front. Obviously, under the conditions of the system studied,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  is kinetically inert, so that replacement of the water ligand with the thiocyanato ligand does not take place<sup>6,11</sup>.

### Extraction of Co(II) and Ni(II)

**Titrimetric determination.** One of the few disadvantages of the use of liquid anion exchangers is the time-consuming back-extraction that is usually necessary in order to complete the determination of an extracted metal ion. In the present study, therefore, a two-phase titration with extractive end-point was used, based on a procedure originally described by Cameron and Gibson<sup>12</sup> for the determination of Co(II), Ni(II), Cr(III) and several other ions. A known excess of EDTA is added to the titration mixture, and back-titration is carried out with standard Co(II) solution, using thiocyanate ions as indicator in the presence of a solution of triphenylarsonium chloride (or tetra-*n*-hexylammonium chloride<sup>13</sup>) in chloroform. At the end-point, a blue ion-association complex is extracted into the organic phase. The results in Fig. 4 indicate that the extraction of Co(II) by Aliquat is quantitative under suitable conditions, so that this inexpensive, technical-grade product can also be used to help indicate the end-point.

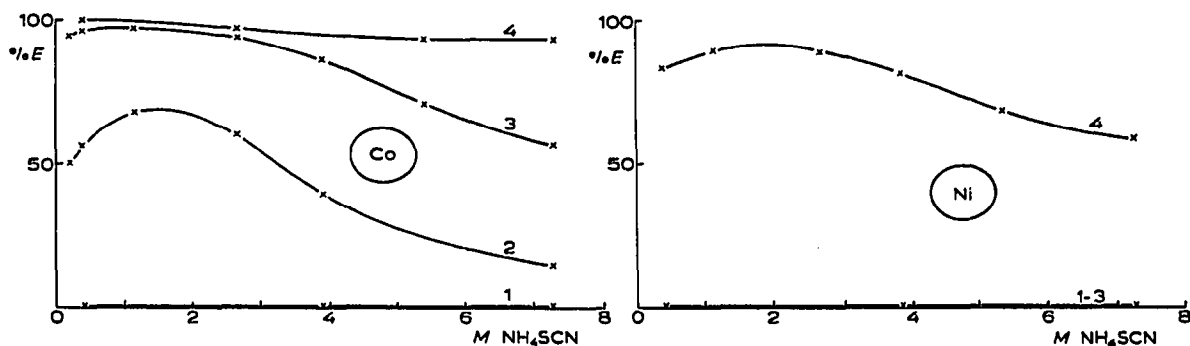


Fig. 4. Percentage extraction versus molarity of  $\text{NH}_4\text{NCS}$  curves for Co(II) and Ni(II). Organic phase: 0.1 M solution of a liquid anion exchanger (thiocyanate form) in toluene. Aqueous phase: 0.02 M Co(II) in  $x$  M  $\text{NH}_4\text{NCS}$  + 0.3 N HCl; 0.02 M Ni(II) in  $x$  M  $\text{NH}_4\text{NCS}$  + 0.02 N HCl. 1, Primenc; 2, Amberlite LA-1; 3, Alamine 336 S; 4, Aliquat 336.

As liquid-liquid extractions are often performed in diluents such as toluene or xylene, which have a lower density than water, the titration procedure forces one to change the composition of the organic phase. This problem is adequately solved by using a solution of Aliquat in carbon tetrachloride, adding this to the organic metal-containing extract in a volume ratio of 1:1. Irrespective of the presence or absence of another liquid anion exchanger, provided it is not too highly coloured, a sharp colour change marks the end-point of the titration.

The complete procedure is as follows. A 5-ml volume of the Co(II)- or Ni(II)-containing organic extract is pipetted into a stoppered erlenmeyer flask. After the addition of 5 ml of a 0.1 M solution of Aliquat (chloride) in carbon tetrachloride, a

known excess of EDTA and 10 ml of 2 *M* potassium thiocyanate solution, dilute ammonia is added until an alkaline reaction is observed. Subsequently, the mixture is shaken for a few minutes in order to effect complexation of the metal ion with EDTA. Back-titration is carried out with a standard Co(II) solution until a permanent light blue colour persists in the organic phase. The mixture must be shaken vigorously near the end-point.

*Extraction and separation.* Results on the extraction of Co(II) and Ni(II) by solutions of each of the four liquid anion exchangers in toluene are presented in Fig. 4. Obviously, the extraction efficiency increases in the same order as the sorption strength in reversed-phase chromatography. This result, which is to be expected on the basis of the relationship  $D = k(1/R_F - 1)$  ( $D$  = distribution coefficient;  $k$  = constant), has amply been verified for, e.g., chloride, bromide and nitrate systems<sup>10</sup>.

It is apparent from Fig. 4 that the extraction of Co(II) by solutions of Alamine is quantitative when suitable acid and thiocyanate concentrations are used, whereas the extraction of Ni(II) is negligible. Therefore, trace amounts of cobalt can be successfully removed from concentrated solutions of nickel salts without any loss of nickel. As the Co(II)-containing complex present in the organic phase has a high molecular extinction coefficient ( $\epsilon_{630} = 1750$ ; see below), the amount of Co(II) present can easily be determined.

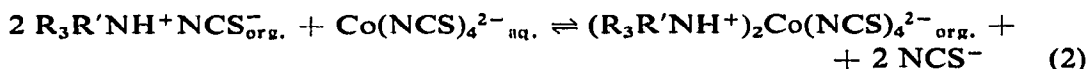
In a typical set of experiments, a 1 *M* solution of nickel chloride in 0.2 *M* ammonium thiocyanate + 0.02 *N* hydrochloric acid, containing  $10^{-2}$ – $10^{-5}$  *M* Co(II), was shaken with an equal volume of a 0.1 *M* solution of AlamineH<sup>+</sup>NCS<sup>-</sup> in toluene. After extraction and phase separation, the spectrum of the organic extract was recorded and the percentage of Co(II) extracted calculated. When using  $10^{-3}$  *M* or even more dilute cobalt solutions, a single extraction suffices for quantitative ( $\geq 99.9\%$ ) removal of cobalt. With  $10^{-2}$  *M* Co(II) solutions, two consecutive extractions are necessary in order to achieve this result. As the detection limit of cobalt can easily be lowered by about an order of magnitude by changing the volume ratio  $V_{\text{org.}}:V_{\text{aq.}}$  to ca. 1:10, liquid-liquid extraction can be used to remove 1– $10^{-4}\%$  of cobalt from nickel salts and determine it quantitatively.

*Nature of the complexes.* Data on the composition of the extracted Co(II)-thiocyanato complex are meagre and, moreover, conflicting. According to Selmer-Olsen<sup>14</sup>, who used triisooctylamine, the extracted species is  $[\text{Co}(\text{SCN})_4]^{2-} \cdot 2 \text{R}_3\text{NH}^+ \cdot 2 \text{R}_3\text{NHCl} \cdot 2 \text{HSCN}$ . Watanabe and Akatsuka<sup>15</sup>, however, on the basis of maximum-loading data, concluded that the blue-coloured species extracted with tri-*n*-octylamine in various diluents is  $(\text{R}_3\text{NH}^+)_2\text{Co}(\text{SCN})_4^{2-}$ . Lastly, Laskorin and Timofeeva<sup>16</sup>, who used the method of continuous variation and of maximum loading, reported that the extracted species has a Co:NCS<sup>-</sup>:amine ratio of 1:2:2.

In this study, the composition of the extracted Co(II)-containing species was determined using both Aliquat and Alamine, as it has occasionally been observed in anion exchanger– $\text{M}^{n+}$ – $\text{X}^-$  systems that additional molecules of exchanger are attached to a tertiary alkylammonium complex metal salt, whereas such a phenomenon is never encountered with substituted quaternary alkylammonium salts (examples:  $\text{Fe}^{3+}$ – $\text{Cl}^-$ ;  $\text{In}^{3+}$ – $\text{Cl}^-$ ;  $\text{UO}_2^{2+}$ – $\text{NO}_3^-$ ; refs. 17–19).

UV-visible spectra of Co(II)-containing extracts show a characteristic absorption band with  $\lambda_{\text{max.}} = 630$  nm and a shoulder at 592 nm. An intense absorption peak at 330 nm, which occurs in the spectra of many metal-thiocyanato complexes,

can most probably be attributed to intraligand transitions<sup>20</sup>. Determination of the ratio  $[\text{Co(II):exchanger}]_{\text{org.}}$  as a function of the aqueous metal ion concentration, the concentrations of the exchanger and (excess)  $\text{NCS}^-$  being kept constant, yields a maximum-loading value of  $1:2.0 \pm 0.1$ , irrespective of the use of Aliquat or Alamine. The same result is obtained when determining the ratio  $\text{Co(II):exchanger}$  of the extracted species by the construction of mole-ratio plots; here, the concentration of the exchanger is increased at constant concentrations of the metal ion and (excess)  $\text{NCS}^-$ . In conclusion, the extraction of  $\text{Co(II)}$  by Aliquat and Alamine may be represented by



thereby confirming Watanabe and Akatsuka's results. As regards the different conclusions reached by Selmer-Olsen, we have re-investigated some of her experiments in our laboratory, the substitution of triisooctylamine by Alamine being the only important change. According to our results, under the conditions used by Selmer-Olsen, the ratio  $\text{Co:amine:NCS}^-$  is indeed 1:4:6. However, instead of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  is present in the organic phase; moreover, maximum loading of the organic phase has not yet been reached. Probably the organic extracts analyzed by Selmer-Olsen contained free  $\text{R}_3\text{NH}^+(\text{NCS}^-, \text{NO}_3^-) \cdot x\text{H}^+(\text{NCS}^-, \text{NO}_3^-)$  next to  $(\text{R}_3\text{NH}^+)_2\text{Co}(\text{NCS})_4^{2-}$ . The rather implausible results obtained by Laskorin and Timofeeva can possibly be explained in an analogous way.

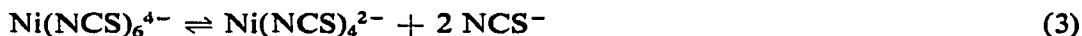
The relatively low extraction efficiency of secondary and primary amines does not allow one to extend the present investigation to Amberlite and Primene. However, the identical shape of the UV-visible spectra of  $\text{Co(II)}$ -containing extracts obtained with all four liquid anion-exchangers demonstrates that the complex metal anion is  $\text{Co}(\text{NCS})_4^{2-}$  in all instances. In this context, it is interesting to note that the molar extinction coefficient  $\epsilon_{630}$  has a value of 1850 in the case of Aliquat, whereas distinctly lower values are obtained with the amines, *e.g.*, 1750 in the case of Alamine. A similar phenomenon has been observed for the exchanger- $\text{Co(II)-Cl}^-$  system<sup>21,22</sup>. Probably the lowering of the  $\epsilon$  values observed is due to a disturbance of the symmetry of the tetracoordinated complex metal ion, caused by the formation of hydrogen bonds of the type  $\text{N-H} \cdots \text{SCN}$  and  $\text{N-H} \cdots \text{Cl}$ .

The study of the nature of the nickel-thiocyanato complex has, for obvious reasons, been limited to systems containing Aliquat. The UV-visible spectra of  $\text{Ni(II)}$ -containing extracts show peaks at 710 and 420 nm, irrespective of the aqueous thiocyanate concentration used in the extraction procedure. These results may be compared with those recorded by De Haas<sup>23</sup> in his study of dilute solutions of nickel thiocyanate in molten dimethylsulphone containing mixtures of potassium and tetrabutylammonium thiocyanate. According to De Haas, both octahedrally and tetrahedrally coordinated nickel-thiocyanato complexes exist in solution, which show absorption peaks at 720 and 400 nm and 670 and 600 nm, respectively. On the basis of his interpretation, we may conclude that in the Aliquat extracts nickel is present as  $\text{Ni}(\text{NCS})_6^{4-}$ .

In a separate set of experiments, it was demonstrated that increasing the polarity of the organic phase by adding (increasing) amounts of, *e.g.*, nitrobenzene or acetophenone to toluene changes the absorption spectrum considerably: the peak at



710 nm gradually disappears, while new peaks emerge at 670 and 630 nm. That is, with increasing polarity of the organic phase, the equilibrium



shifts to the right.

The extraction efficiency of solutions of Aliquat in toluene towards nickel is small compared with that towards cobalt (see the legend to Fig. 4). Moreover, usually this efficiency strongly decreases when increasing polarity of the organic phase. Therefore, the maximum-loading and the mole-ratio techniques are of limited value in the Aliquat–Ni(II)–NCS<sup>−</sup> system. As a consequence, no quantitative correlation has yet been established between the percentage of more polar solvent added to toluene and the value of the ratio Ni(NCS)<sub>6</sub><sup>4−</sup>:Ni(NCS)<sub>4</sub><sup>2−</sup>.

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