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Solvent Extraction of Cobalt(II) and Nickel(II) by a Quaternary Ammonium Thiocyanate

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Abstract

The solvent extraction of cobalt(II) and nickel(II) into xylene solutions of a quaternary ammonium thiocyanate ($R_4N.NCS$) has been investigated and shown to depend markedly upon the identity of the counteranion (X^-) present in the aqueous phase. The extent of extraction of both metals increases with increasing stability of the corresponding ion-pair, $R_4N.X$. The dependence of metal distribution upon the concentrations of $R_4N.NCS$, $R_4N.X$, and X^- is consistent with the extraction of cobalt from sulfate ($X^- = \frac{1}{2}SO_4^{2-}$), chloride ($X^- = Cl^-$), bromide ($X^- = Br^-$), and nitrate ($X^- = NO_3^-$) media according to the stoichiometry

$$Co^{2+} + 2X^- + 4R_4N.NCS = (R_4N)_2Co(NCS)_4 + 2R_4N.X$$

The importance of certain deviations from ideal behavior, namely association of the extractant in the organic phase and $CoSO_4$ ion-pair formation in the aqueous phase, has been demonstrated. Examination of the electronic spectra of the organic extracts reveals that cobalt is extracted as the tetrahedral anion $Co(NCS)_4^{2-}$ while nickel forms an octahedral complex, probably $Ni(NCS)_4(H_2O)_2^{2-}$. Addition of *n*-octylamine ($R.NH_2$) to the thiocyanate extractant enhances the extraction of nickel, and spectroscopic data are consistent with the existence of the equilibrium

$$Ni(NCS)_4(H_2O)_2^{2-} + 2R.NH_2 = Ni(NCS)_4(R.NH_2)_2^{2-} + 2H_2O$$

The extraction of cobalt(II) from aqueous thiocyanate solutions by alkylammonium thiocyanates ($R_4N.NCS$) has been investigated, both as an analytical procedure (*1–4*) and in fundamental solvent extraction studies (*5–8*). In addition, a proprietary process has been developed in which the use of such an extractant is proposed for the removel of cobalt from nickel sulfate solutions, either in the presence (*9*) or in the absence of thiocyanate ion in the aqueous phase (*10, 11*). Although extraction efficiencies are high in the presence of added aqueous thiocyanate (*7–9*), much lower metal loadings are obtained from solutions containing sulfate as the only anion (*9–11*). Similarly, the extraction of nickel(II) is very low from sulfate solutions (*9–11*), but is greatly enhanced in the presence of aqueous thiocyanate (*7, 8, 12*).

The extraction of cobalt from thiocyanate media has been shown (*6–8*) to proceed according to

$$Co^{2+} + 2NCS^- + 2R_4N.NCS = (R_4N)_2Co(NCS)_4 \quad (1)$$

(In this and the following equations, ionic species are present in the aqueous phase, and uncharged species are present in the organic phase.) It has been suggested (*4, 11*), without experimental confirmation, that extraction from sulfate media is described by

$$Co^{2+} + SO_4^{2-} + 4R_4N.NCS = (R_4N)_2Co(NCS)_4 + (R_4N)_2SO_4 \quad (2)$$

In this paper we report the results of an investigation into the effect of various aqueous anions (thiocyanate, iodide, bromide, chloride, flouride, nitrate, perchlorate, sulfate, and acetate) upon the extraction of cobalt(II) and nickel(II) by the quaternary ammonium thiocyanate derived from Aliquat 336 (commerical tricaprylmethylammonium chloride manufactured by Henkel Corp.).

EXPERIMENTAL

Preparation and Analysis of Aliquat 336 Thiocyanate

A solution of Aliquat 336 (25 g) in xylene (500 mL) was washed with 0.1 *M* hydrochloric acid (3 × 500 mL) and then with water (2 × 500 mL). This treatment effected the removal of traces of iron, which, if allowed to remain, caused a red color to develop in the organic phase when it was converted to the thiocyanate form. The purified Aliquat 336 solution was contacted with 0.1 *M* ammonium thiocyanate (2 × 500 mL) and washed with water (5 × 500 mL). Water dispersed in the organic phase was removed by filtration, and the resulting solution of Aliquat 336 thiocyanate (~0.1 *M*) was diluted with xylene as required for the extraction experiments. The thiocyanate content of the extractant was determined by contacting a sample (10 mL) diluted with xylene (15 mL) with 1.0 *M* ammonium perchlorate solution (25 mL), and titrating the thiocyanate displaced into the aqueous phase against standard silver nitrate solution, using a potentiometric method with silver and mercurous sulfate electrodes.

Measurement of Anion Exchange Constants for Aliquat 336 Salts

The exchange constants for

$$R_4N.Y + X^- = R_4N.X + Y^- \qquad (3)$$

where X^- and Y^- are taken from the group NCS^-, I^-, Br^-, Cl^-, F^-, NO_3^-, ClO_4^-, $CH_3.COO^-$, and $\frac{1}{2}SO_4^{2-}$, were determined by contacting 0.02 *M* solutions of the salts $R_4N.X$ (prepared by metathesis from the chloride) in xylene with equal volumes of aqueous solutions of the required ammonium salt NH_4Y in the range 0.01 to 0.50 *M* at 20°C. The phases were allowed to separate, the aqueous phase was filtered to remove entrained organic phase, and the halide or thiocyanate (which may be X^- or Y^-) content was determined by potentiometric titration against standard silver nitrate solution.

Metal Distribution Experiments

Stock solutions (0.020 *M*) of cobalt(II) and nickel(II) salts were prepared from AR grade products and analyzed for metal content by addition of excess pyridine and standard ammonium thiocyanate to precipitate $M(C_5H_5N)_4(NCS)_2$ (where M = Co or Ni). The residual thiocyanate was determined by potentiometric titration against standard silver nitrate solution. Distribution experiments were carried out by contacting solutions of Aliquat 336 thiocyanate in xylene (0.001 to 0.100 *M*) with 0.001 *M* cobalt(II) or nickel(II) in various ammonium salt solutions in the range 0.00 to 2.00 *M*. An equilibration time of 2 min was allowed at 20°C, the phases were allowed to separate for 1 h, and the organic phase was clarified by filtration. Cobalt contents of organic phases were determined by measurement of the absorbance at 625 nm against a xylene blank. It was shown by a separate series of experiments that quantitative extraction of cobalt is obtained from aqueous phases containing 0.1 *M* ammonium thiocyanate, and that Beer's law is obeyed up to at least 0.001 *M* cobalt in the organic phase. Extracts from such aqueous phases containing accurately known concentrations of cobalt (0.0001 to 0.001 *M*) were used to prepare a calibration plot. Nickel contents of aqueous phases were determined by atomic absorption spectrophotometry.

Measurement of Activity Coefficients

Apparent molalities of solutions of Aliquat 336 thiocyanate prepared in *p*-xylene (Merck, zur Synthese grade) were determined by measurement of the freezing-point depression of the solvent and comparison with the values obtained for known concentrations of naphthalene or benzophenone. The latter solutes were found to exhibit ideal behavior up to at least 0.1 *m*. Thiocyanate contents of organic phases were determined by titrating weighed samples dissolved in ethanol against standard silver nitrate. Molal activity coefficients of the extractant ($y_{R_4N.NCS}$) were calculated for each concentration by means of the relation

$$y_{R_4N.NCS} = \frac{\text{molality with respect to freezing-point depression}}{\text{molality with respect to thiocyanate content}}$$

As a check on the purity of the Aliquat 336 thiocyanate, some experiments were carried out with synthetic methyl tri-*n*-octylammonium thiocyanate. The latter compound was prepared by heating tri-*n*-octylamine (Riedel-de Haen, prosynth grade) with iodomethane, dissolving the thus formed quaternary ammonium iodide in *p*-xylene and contacting the solution repeatedly with aqueous ammonium thiocyanate solution.

RESULTS AND DISCUSSION

Anion Exchange Constants for Aliquat 336 Salts

The proposed mechanism of extraction of cobalt(II) from sulfate media, Eq. (2), suggests that extraction in the presence of an anion X^- can be expressed in the general form

$$Co^{2+} + 2X^- + 4R_4N.NCS = (R_4N)_2Co(NCS)_4 + 2R_4N.X \quad (4)$$

Equation (4) is seen to consist of a summation of the equations for extraction in the presence of aqueous thiocyanate, Eq. (1), and that for the anion-exchange reaction:

$$2R_4N.NCS + 2X^- = 2R_4N.X + 2NCS^- \tag{5}$$

Accordingly, it should be possible to relate the efficiency of metal extraction from a given aqueous phase to the extent to which the Exchange Reaction (5) will proceed under the pertaining conditions. Table 1 lists the experimentally determined concentration constants, $K_{x,y}$, for Eq. (3), and Table 2, the concentration constants, $K_{x,NCS}$, for Eq. (5), derived either directly from the data in Table 1 or by the combination of two or more of the measured constants.

With the exception of the chloride–sulfate system, relatively consistent values were obtained for each of the exchange constants throughout the range of concentrations investigated, despite the fact that the experiments were not conducted at constant ionic strength and that concentrations rather than activities were used in the calculations. Since the variation in activity coefficients (y) among the univalent anions studied is small at any given ionic strength, it is evident that they will largely cancel out in expressions such as

$$K'_{NO_3,NCS} = [R_4N.NO_3]y_{NCS}[NCS^-][R_4N.NCS]^{-1}y_{NO_3}^{-1}[NO_3^-]^{-1} \tag{6}$$

In the case of the divalent sulfate ion, however, the activity coefficients are very much lower than those for corresponding concentrations of a univalent

TABLE 1

Concentration Equilibrium Constants ($K_{x,y}$) for the Reaction

$R_4N.Y + X^- = R_4N.X + Y^-$

		$K_{x,y}$ at initial aqueous molarity of Y					
Y	X	0.50	0.20	0.10	0.05	0.02	0.01
NCS	ClO_4	—	—	—	11.4	12.4	10.8
NCS	I	—	—	—	0.20	0.22	0.23
NCS	NO_3	0.010	0.010	0.010	—	—	—
I	NO_3	0.037	0.041	0.042	—	—	—
NO_3	Cl	0.034	0.023	0.030	—	—	—
Br	NO_3	—	3.44	3.36	3.17	3.13	3.04
Cl	$\frac{1}{2}SO_4$	0.61	0.69	0.79	0.89	1.06	1.20
Cl	CH_3COO	0.071	0.071	0.068	0.066	0.068	—
Cl	F	0.028	0.029	0.026	0.026	0.028	—

TABLE 2

Concentration Equilibrium Constants ($K_{x,NCS}$) for the Reaction

$$2R_4N.NCS + 2X^- = 2R_4N.X + 2NCS^-$$

X	$pK_{x,NCS}$
ClO_4	−2.12
NCS	0.00
I	1.32
NO_3	4.00
Br	5.02
Cl	7.08
$\frac{1}{2}SO_4$	7.17
CH_3COO	9.41
F	10.20

anion. The wide variation in the value of the chloride–sulfate exchange constant over the concentration range studied is probably mainly attributable to this effect. Thus, while the value of the concentration constant changes from 0.61 to 1.20 in the range 0.50 to 0.01 *N* aqueous sulfate (mean value 0.87 ± 0.18, 20.4% relative mean deviation), when literature values of sulfate ion activities (*13*) are incorporated, a range of only 1.06 to 1.29 is observed (mean value 1.13 ± 0.08, 7.4% relative mean deviation).

The equilibrium constants for Eq. (5) given in Table 2 show that the anions investigated displace thiocyanate ion from Aliquat 336 thiocyanate in the order $ClO_4^- > NCS^- > I^- > NO_3^- > Br^- > Cl^- > SO_4^{2-} > CH_3.COO^- > F^-$.

Effect of the Aqueous Anion on Metal Extraction

The extraction of cobalt(II) and nickel(II) by Aliquat 336 thiocyanate in the presence of various ammonium salts (0.10 *M* NH_4X) is shown in Figs. 1 and 2, respectively. In each case the extraction of cobalt greatly exceeds that of nickel, and for both metals the extraction efficiency varies according to the anion present, and lies in the order $NCS^- > I^- > NO_3^- > Br^- > Cl^- > SO_4^{2-} > CH_3COO^- > F^-$. Perchlorate is omitted from the list since its position in the order depends upon the concentration of extractant. However, for the remaining anions the order of metal extraction is the same as that for the thiocyanate displacement reaction, Eq. (5). This observation supports the validity of the assumed general extraction reaction, Eq. (4), and of its interpretation as the summation of Eqs. (1) and (5), and suggests that the

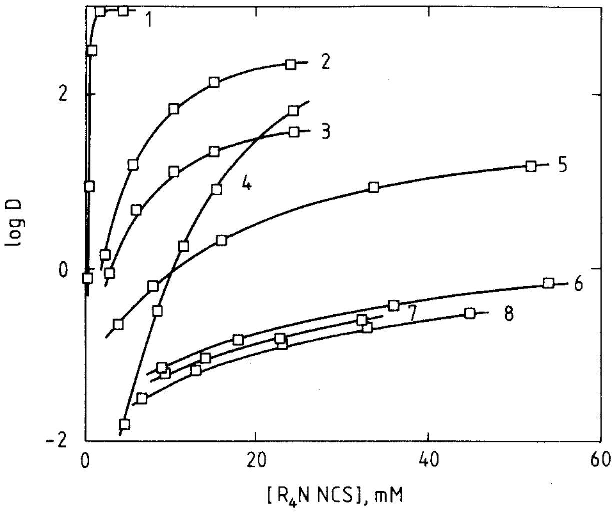

FIG. 1. Extraction of cobalt(II) from 0.1 *M* ammonium salt (NH_4X) solutions by Aliquat 336 thiocyanate in xylene. X^-: (1) NCS^-, (2) I^- and NO_3^-, (3) Br^-, (4) ClO_4^-, (5) Cl^-, (6) $\frac{1}{2}SO_4^{2-}$, (7) CH_3COO^-, and (8) F^-.

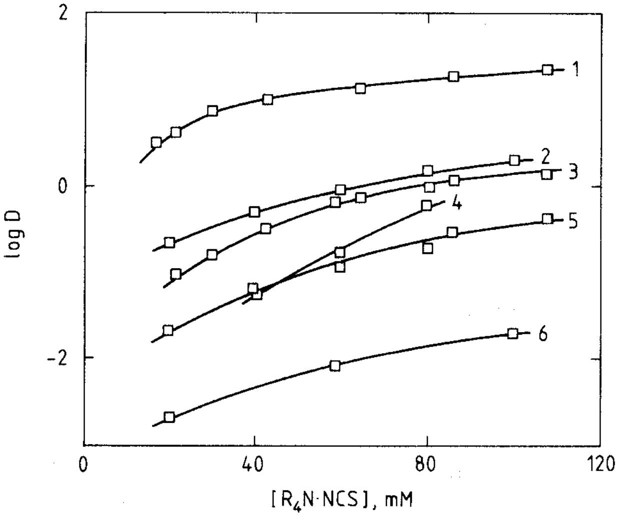

FIG. 2. Extraction of nickel(II) from 0.1 *M* ammonium salt (NH_4X) solutions by Aliquat 336 thiocyanate in xylene. X^-: (1) NCS^-, (2) I^-, (3) NO_3^-, (4) ClO_4^-, (5) Br^-, and (6) Cl^-.

extent of extraction of a given metal from aqueous NH_4X media depends largely upon the stability of the $R_4N.X$ ion pair formed during extraction, relative to that of the extractant, $R_4N.NCS$. The anomalous behavior of perchlorate can be explained by the fact that this anion actually forms a more stable ion pair with the Aliquat cation than does thiocyanate (Table 1, $K_{ClO_4,NCS} = 11.5 \pm 0.6$), with the result that at low concentrations of extractant almost all the thiocyanate will be displaced into the aqueous phase:

$$R_4N.NCS + ClO_4^- = R_4N.ClO_4 + NCS^- \quad (7)$$

Hence there remain, at equilibrium, negligible amounts of the Aliquat thiocyanate required for metal extraction. As the initial concentration of extractant is increased, however, displacement of thiocyanate into the aqueous phase becomes less complete, and residual Aliquat thiocyanate is available for metal extraction. In confirmation of the above, it was observed that cobalt extracted into Aliquat 336 thiocyanate was completely back-extracted by contact with 1.0 *M* ammonium perchlorate solution.

Extraction of Cobalt from Sulfate Media

The equilibrium constant for the proposed reaction in the extraction of cobalt(II) from sulfate media, Eq. (2), is given by the equation

$$K_{ex} = [(R_4N)_2Co(NCS)_4][(R_4N)_2SO_4][Co^{2+}]^{-1}[SO_4^{2-}]^{-1}[R_4N.NCS]^{-4} \quad (8)$$

from which the following expression can be derived:

$$\log D + \log [(R_4N)_2SO_4] = \log K_{ex} + \log [SO_4^{2-}] + 4 \log [R_4N.NCS] \quad (9)$$

where the distribution coefficient

$$D = [(R_4N)_2Co(NCS)_4][Co^{2+}]^{-1} \quad (10)$$

Inspection of Eq. (9) shows that a plot of $\log D + \log [(R_4N)_2SO_4]$ against $\log [R_4N.NCS]$ at constant $[SO_4^{2-}]$ should have a slope of 4.0. Such plots for the extraction of cobalt from ammonium sulfate solutions in the concentration range 0.001 to 0.500 *M* form a series of straight lines with slopes increasing from 2.10 at 0.001 *M* to 2.80 at 0.500 *M* aqueous sulfate. At low initial concentrations of ammonium sulfate, the constant $[SO_4^{2-}]$ condition is not met, since an amount of sulfate equivalent to the cobalt extracted is removed from the aqeuous phase in each case, thereby causing the observed slopes to differ considerably from the ideal value. At high concentrations of ammonium sulfate (e.g., 0.500 *M*), however, the amount of sulfate co-extracted with the cobalt (i.e., a maximum of 0.001 *M*) is negligible compared with that remaining in the aqueous phase. Accordingly, under such conditions, slopes closer to the ideal value are observed; the remaining discrepancy is probably attributable to deviations from ideal behavior caused by association of the extractant in the organic phase. Such deviations from ideality can be taken into account if the extractant concentration, $[R_4N.NCS]$ in Eq. (9) is replaced by the corresponding activity, $\{R_4N.NCS\}$, calculated from the expression

$$\{R_4N.NCS\} = y_{R_4N.NCS}[R_4N.NCS] \tag{11}$$

using the activity coefficients $y_{R_4N.NCS}$ (Fig. 3) determined by cryoscopy. Plots of $\log D + \log [(R_4N)_2SO_4]$ against $\log \{R_4N.NCS\}$ at constant $[SO_4^{2-}]$ are shown in Fig. 4 to disclose slopes of the theoretical value, 4.0.

With regard to the dependence of cobalt distribution upon aqueous sulfate concentration, Eq. (9) requires that, at constant $[R_4N.NCS]$, plots of log

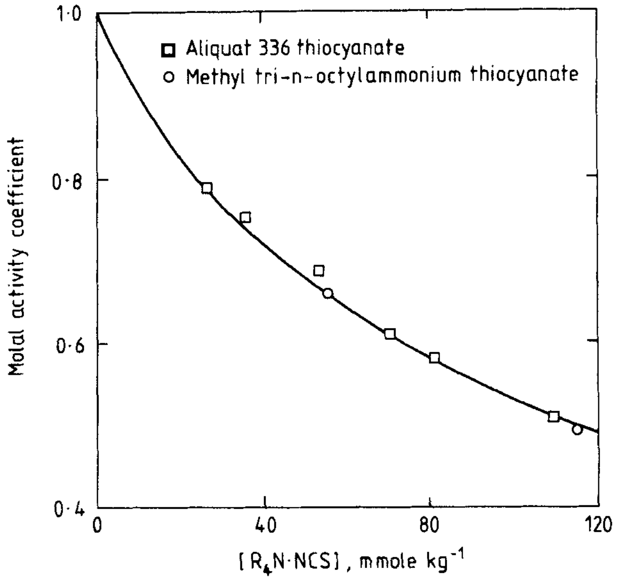

FIG. 3. Molal activity coefficients for Aliquat 336 thiocyanate and methyl tri-*n*-octylammonium thiocyanate in *p*-xylene at 13°C.

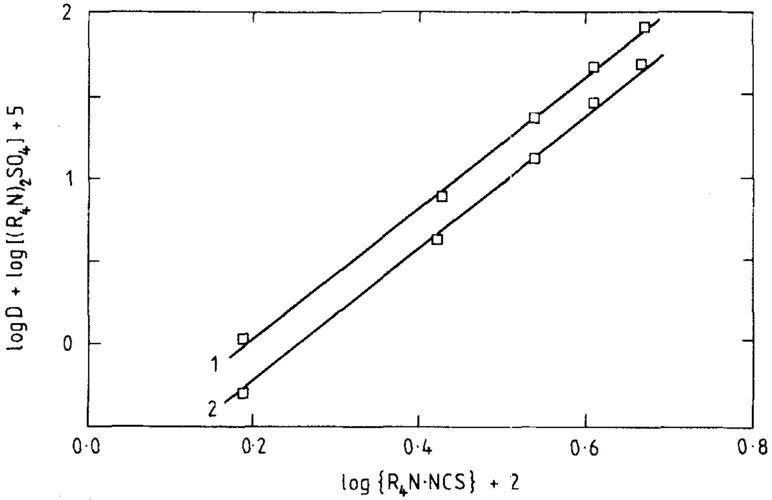

FIG. 4. Extraction of cobalt(II) from ammonium sulfate solutions by Aliquat 336 thiocyanate in xylene: (1) 0.12 *M* $(NH_4)_2SO_4$ and (2) 0.50 *M* $(NH_4)_2SO_4$.

$D + \log [(R_4N)_2SO_4]$ against $\log [SO_4^{2-}]$ should give straight lines of unit slope. However, the experimental data show the unexpected result that cobalt extraction reaches a maximum at about 0.05 *M* aqueous sulfate and decreases at sulfate concentrations higher than this value (Fig. 5). This behavior can be rationalized by consideration of the formation in the aqueous phase of the cobalt sulfate ion-pair

$$Co^{2+} + SO_4^{2-} = CoSO_4 \qquad (12)$$

the formation constant of which has been determined as 295 at 25°C and zero ionic strength (*14*). This aqueous phase reaction competes with the extraction process for the available cobalt(II) ion, with the result that the distribution coefficient must be redefined as

$$D = [(R_4N)_2Co(NCS)_4]([Co^{2+}] + [CoSO_4])^{-1} \qquad (13)$$

since the aqueous phase contains both Co^{2+} and $CoSO_4$ species. Substitution of the relation

$$[CoSO_4] = K[Co^{2+}][SO_4^{2-}] \qquad (14)$$

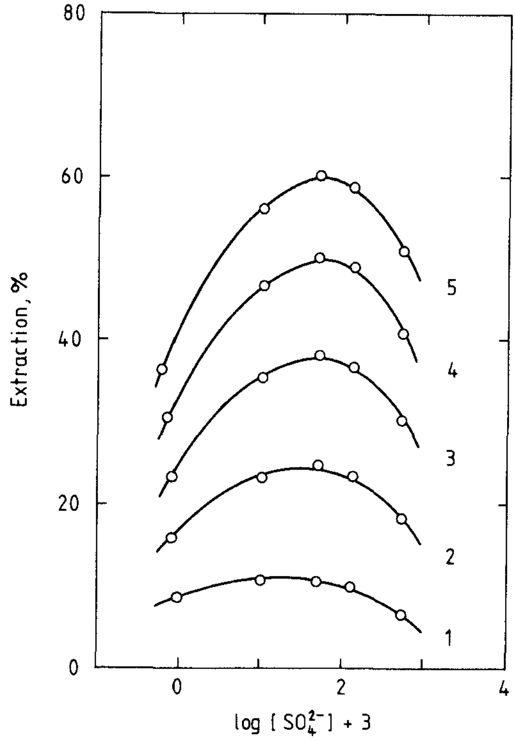

FIG. 5. Extraction of cobalt(II) from ammonium sulfate solutions by Aliquat 336 thiocyanate in xylene. Concentrations of extractant: (1) 0.019, (2) 0.037, (3) 0.056, (4) 0.075, and (5) 0.094 *M*.

where K is the formation constant of $CoSO_4$, into Eq. (13) gives the relation

$$D = [(R_4N)_2Co(NCS)_4][Co^{2+}]^{-1}(1 + K[SO_4^{2-}])^{-1} \qquad (15)$$

Substitution of Eq. (15) into Eq. (8) then allows the following expression to be derived:

$$\log D + \log(1 + K[SO_4^{2-}]) + \log[(R_4N)_2SO_4] = \log K_{ex} + 4\log[R_4N.NCS] + \log[SO_4^{2-}] \qquad (16)$$

Equation (16) requires that plots of $\log D + \log(1 + K[SO_4^{2-}]) + \log[R_4N)_2SO_4]$ against $\log[SO_4^{2-}]$ at constant $[R_4N.NCS]$ should yield

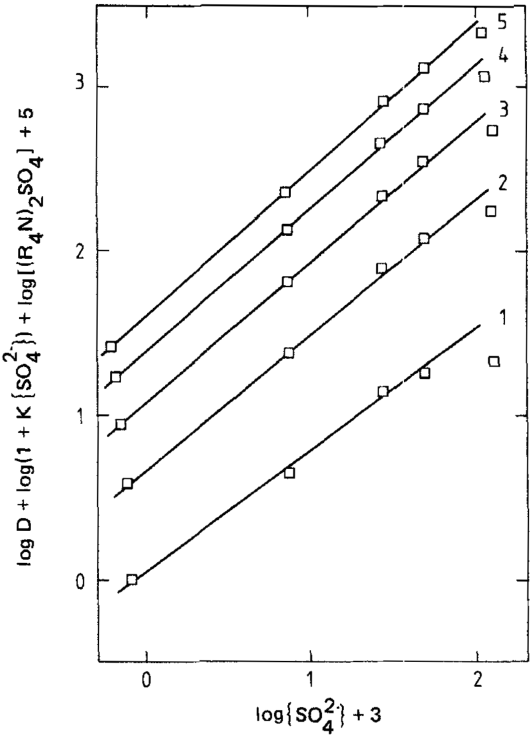

FIG. 6. Extraction of cobalt(II) from ammonium sulfate solutions by Aliquat 336 thiocyanate in xylene. Concentrations of extractant as in Fig. 5. Slopes of curves: (1) 0.74, (2) 0.84, (3) 0.87, (4) 0.88, and (5) 0.90.

straight lines of unit slope. This is examined in Fig. 6, using sulfate ion activities (*13*), rather than concentrations, in view of the high ionic strengths involved. Slopes close to unity are displayed, particularly at high extractant concentrations, where the constant [R$_4$N.NCS] condition is most closely met.

Rearrangement of Eq. (9) to the form

$$\log D = \log K_{ex} + \log[SO_4^{2-}] + 4\log[R_4N.NCS] - \log[(R_4N)_2SO_4] \quad (17)$$

shows that, at constant [SO$_4^{2-}$] and [R$_4$N.NCS], a plot of log D against log [(R$_4$N)$_2$SO$_4$] should reveal a slope of −1.0. This is examined in Fig. 7 for the extraction of cobalt(II) sulfate from 0.05 M ammonium sulfate using Aliquat 336 thiocyanate (0.08 and 0.12 M) to which varying amounts of Aliquat 336

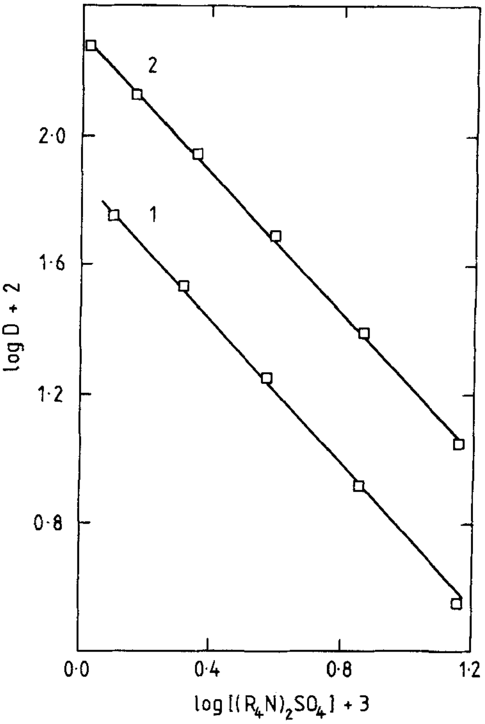

FIG. 7. Extraction of cobalt from 0.05 *M* ammonium sulfate by Aliquat 336 thiocyanate in the presence of Aliquat 336 sulfate in xylene. Concentrations of Aliquat 336 thiocyanate: (1) 0.08 and (2) 0.12 *M*.

sulfate (0.00 to 0.016 *M*) had been added. Slopes close to the theoretical value are displayed.

Extraction of Cobalt from Nitrate, Chloride, and Bromide Media

The proposed reaction for the extraction of cobalt in the presence of univalent anions (Eq. 4, $X^- = NO_3^-$, Cl^-, or Br^-) can be used to derive the relationship

$$\log D + 2\log[R_4N.X] = \log K_{ex} + 2\log[X^-] + 4\log[R_4N.NCS] \qquad (18)$$

Slope analysis treatments similar to those described above for sulfate were applied. In the case of these univalent anions, however, cobalt extraction is appreciable even at very low concentrations of extractant (i.e., less than 0.01 *M*). Accordingly, the activity coefficients of the extractant are close to unity and plots of $\log D + 2 \log [R_4N.X]$ against $\log [R_4N.NCS]$, shown in Fig. 8, exhibit slopes of the theoretical value, 4.0.

The dependence of cobalt distribution upon the concentration of the aqueous anion was examined by use of an expression analogous to that derived for sulfate media, namely

$$\log D + \log (1 + K[X^-]) + 2 \log [R_4N.X] = \log K_{ex} + 4 \log [R_4N.NCS] + 2 \log [X^-] \qquad (19)$$

The aqueous phase complexation reaction for univalent anions,

$$Co^{2+} + X^- = CoX^+ \qquad (20)$$

is less important than in the case of sulfate, as shown by the low values of the formation constants for Eq. (20): 4.9 ($X^- = Cl^-$) (*15*), 0.74 ($X^- = Br^-$) (*16*), and 0.00 ($X^- = NO_3^-$). Distribution plots based on Eq. (19), using the appropriate activity coefficients for ammonium salts (*13*), are shown in Fig. 9. Additions of the corresponding Aliquat 336 salt, $R_4N.X$, were made to the organic phase in these experiments in order to suppress extraction sufficiently to avoid the errors associated with the measurement of very high

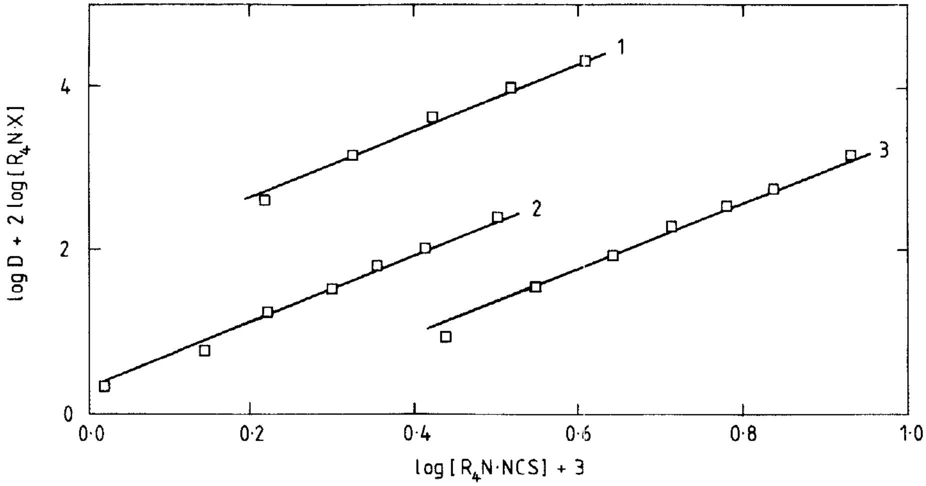

FIG. 8. Extraction of cobalt(II) from ammonium salt (NH_4X) solutions by Aliquat 336 thiocyanate in xylene. (1) 0.1 *M* NH_4NO_3, (2) 1.0 *M* NH_4Cl, and (3) 0.1 *M* NH_4Br.

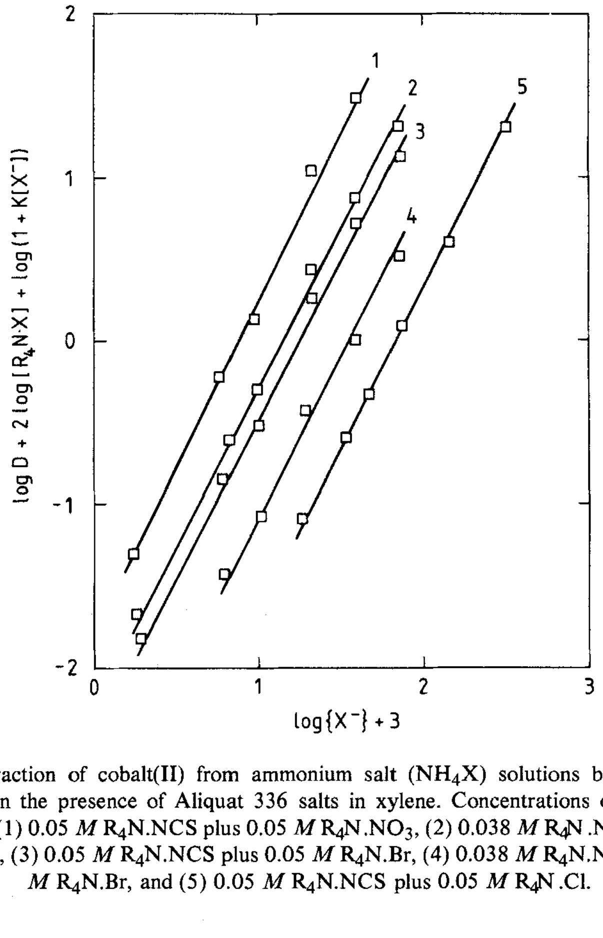

FIG. 9. Extraction of cobalt(II) from ammonium salt (NH_4X) solutions by Aliquat 336 thiocyanate in the presence of Aliquat 336 salts in xylene. Concentrations of Aliquat 336 thiocyanate: (1) 0.05 *M* $R_4N.NCS$ plus 0.05 *M* $R_4N.NO_3$, (2) 0.038 *M* $R_4N.NCS$ plus 0.062 *M* $R_4N.NO_3$, (3) 0.05 *M* $R_4N.NCS$ plus 0.05 *M* $R_4N.Br$, (4) 0.038 *M* $R_4N.NCS$ plus 0.062 *M* $R_4N.Br$, and (5) 0.05 *M* $R_4N.NCS$ plus 0.05 *M* $R_4N.Cl$.

distribution coefficients. In all cases, slopes close to the theoretical value (2.0) were obtained.

Rearrangement of Eq. (18) to the form

$$\log D - 4 \log [R_4N.NCS] - 2 \log [X^-] = \log K_{ex} - 2 \log [R_4N.X] \qquad (21)$$

shows that plots of $\log D - 4 \log [R_4N.NCS] - 2 \log [X^-]$ against $\log [R_4N.X]$ should display slopes of −2.0. This is examined in Fig. 10 for the extraction of cobalt(II) from chloride, bromide, and nitrate media. The slopes obtained, −1.8 to −2.4, are reasonably close to the expected value in view of the fact that it is not possible to take into account the effects of extractant association in these complex ($R_4N.NCS$–$R_4N.X$) organic phases.

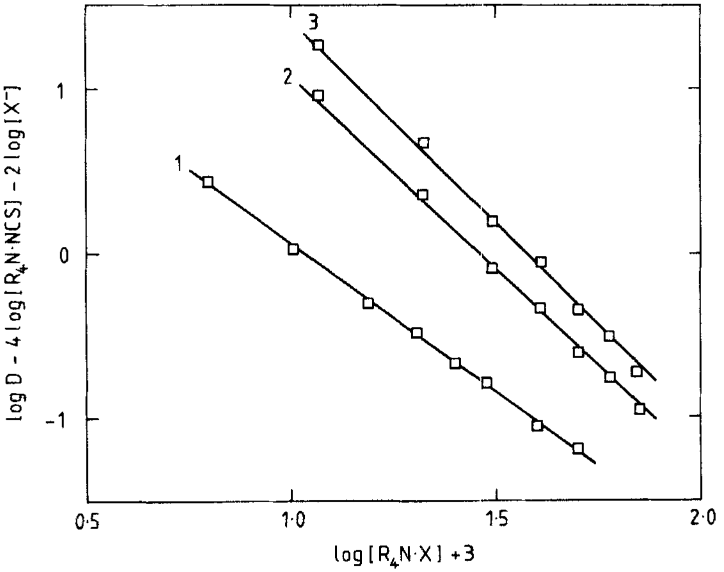

FIG. 10. Extraction of cobalt(II) from ammonium salt (NH_4X) solutions by Aliquat 336 thiocyanate in the presence of Aliquat 336 salts in xylene. (1) Extraction from 0.04 *M* NH_4Cl by 0.050 *M* $R_4N.NCS$, (2) extraction from 0.025 *M* NH_4Br by 0.030 *M* $R_4N.NCS$, and (3) extraction from 0.01 *M* NH_4NO_3 by 0.030 *M* $R_4N.NCS$. Slopes of curves: (1) 1.8, (2) 2.3, and (3) 2.4.

Extraction of Nickel from Nitrate and Bromide Media

The extraction of nickel(II) by Aliquat 336 thiocyanate is less amenable to study than that of cobalt(II) on account of the low levels of nickel extraction encountered. However, the data for the extraction of nickel from nitrate and bromide media are consistent with an extraction stoichiometry analogous to that found for cobalt, Eq. (4), since plots of log $D + 2$ log $[R_4N.X]$ against $\{R_4N.NCS\}$, shown in Fig. 11, reveal slopes of the theoretical value (4.0). In these experiments the equilibrium values of $[R_4N.X]$ were calculated by use of the appropriate anion exchange constants, $K_{x,NCS}$, and activities of Aliquat 336 were calculated from the cryoscopic data on account of the high concentrations (0.02 to 0.11 *M*) of the extractant used.

Structures of Extracted Metal Complexes

Aqueous solutions of cobalt(II) in the absence of complex-forming anions show a pink color characteristic of the octahedral species $Co(H_2O)_6^{2+}$ due to

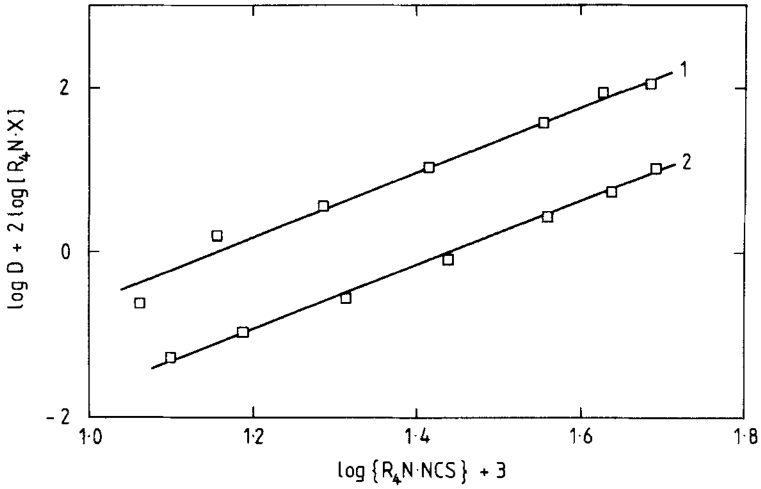

FIG. 11. Extraction of nickel(II) from ammonium salt (NH_4X) solutions by Aliquat 336 thiocyanate in xylene. Extraction from (1) 0.10 *M* NH_4NO_3 and (2) 0.10 *M* NH_4Br.

a weak absorption band ($\varepsilon = 5$) at 512 nm (Fig. 12, Curve 1). The addition of large amounts of thiocyanate causes the development of a blue color due to strong absorption at 620 nm ($\varepsilon = 200$ in 5 *M* and $\varepsilon = 400$ in 10 *M* NH_4NCS) and characteristic of tetrahedral coordination (*17*). Some of the hexaquo cation persists in such solutions, however, as evidenced by a shoulder at 510 nm in these spectra (Fig. 12, Curve 2). The elimination of solvent water as a competing ligand causes more complete formation of the tetrahedral complex, as shown by the spectrum of cobalt(II) nitrate hexahydrate (0.001 *M*) plus ammonium thiocyanate (0.010 *M*) in anyhdrous acetone ($\varepsilon = 1890$ at 625 nm). Comparison with the absorption spectrum for cobalt(II) extracted from 0.1 *M* NH_4NCS into 0.02 *M* Aliquat 336 thiocyanate in xylene reveals that the intense blue organic extract ($\varepsilon = 1860$ at 625 nm) also contains a tetrahedral complex, in agreement with the stoichiometry $(R_4N)_2Co(NCS)_4$ deduced from the metal distribution data.

The absorption spectrum of nickel(II) perchlorate in 10 *M* NH_4NCS is shown in Fig. 13. The solution exhibits the pale green color typical of octahedrally coordinated nickel(II); the absorption bands are situated at wavelengths close to those for the hexaquo nickel(II) cation, but with some sixfold increase in intensity. The spectrum for nickel(II) extracted from 1.0 *M* NH_4NCS into 0.10 *M* Aliquat 336 thiocyanate shows that the extracted complex retains the features of octahedral symmetry. The unexpectedly high intensity of the absorption at 425 nm is largely due to tailing of the adjacent

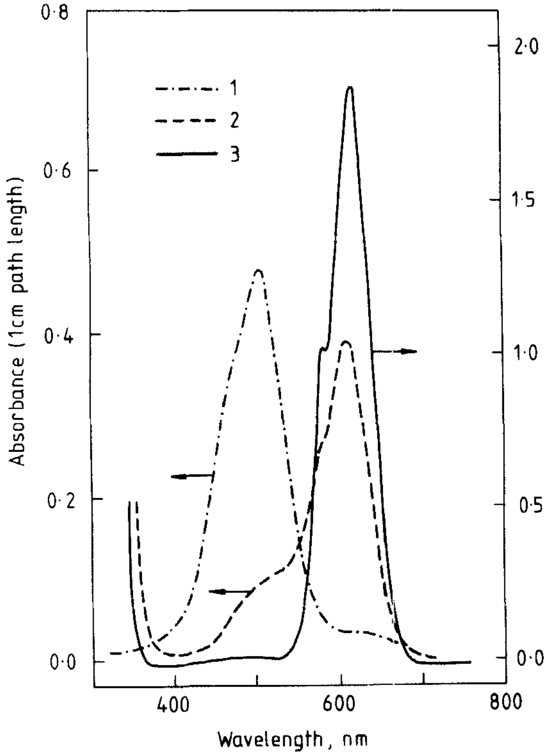

FIG. 12. Electronic spectra of cobalt(II) solutions. (1) 0.10 *M* $Co(ClO_4)_2$ in water, (2) 0.002 *M* $Co(ClO_4)_2$ in 5.0 *M* NH_4NCS in water, and (3) 0.001 *M* $Co(NO_3)_2$ in 0.010 *M* NH_4NCS in acetone and (same curve) 0.001 *M* cobalt(II) extracted from 0.10 *M* NH_4NCS into 0.02 *M* Aliquat 336 thiocyanate in xylene.

charge-transfer band ($\varepsilon = 3000$) at 348 nm. In contrast, solutions of nickel(II) nitrate hexahydrate plus ammonium thiocyanate in anhydrous acetone (Fig. 13) show a deep blue color, which indicates that under such conditions—the blue color is discharged by the addition of water—a complex of tetrahedral symmetry can exist (*18*). We have been unable to confirm the reported existence (*7*) of such a species in the organic extracts from concentrated aqueous nickel(II) solutions, however. It appears, therefore, that the extracted complex in the case of nickel contains an octahedral $Ni(NCS)_4(H_2O)_2^{2-}$ entity, and that the poor extractability of the nickel complex compared with that of cobalt is due to the greater secondary aquation of the former resulting from the presence of the two coordinated

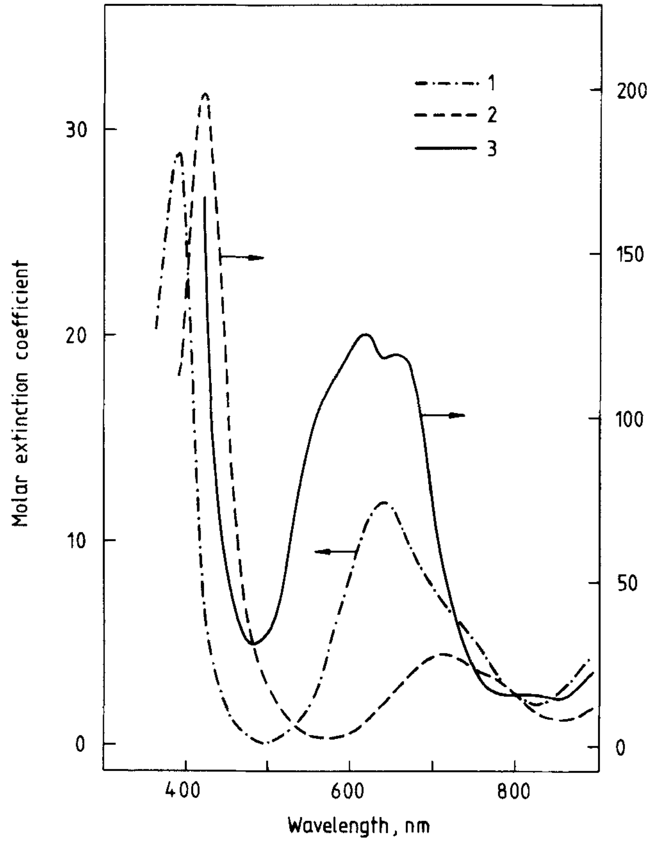

FIG. 13. Electronic spectra of nickel(II) solutions. (1) 0.02 *M* $Ni(ClO_4)_2$ in 10.0 *M* NH_4NCS in water, (2) 0.002 *M* nickel(II) extracted from 1.0 *M* NH_4NCS into 0.10 *M* Aliquat 336 thiocyanate in xylene, and (3) 0.007 *M* $Ni(NO_3)_2$ in 0.070 *M* NH_4NCS in acetone.

water molecules. Further, it might be expected that with, for example, nitrogen-donor ligands such as amines ($R.NH_2$), equilibria such as

$$Ni(NCS)_4(H_2O)_2^{2-} + 2R.NH_2 = Ni(NCS)_4(R.NH_2)_2^{2-} + 2H_2O \quad (22)$$

could exist, replacement of the water molecules in the nickel complex by the hydrophobic amine entities thereby enhancing the extractability of the metal. This hypothesis was tested by addition of *n*-octylamine (0.01 *M*) to Aliquat 336 thiocyanate (0.02 to 0.06 *M*) and comparison of the extraction of nickel from 0.1 *M* NH_4X solutions with that found in the absence of the amine. The data are exemplified by the results for bromide media, from which extractions of 26, 45, and 59% were observed for 0.02, 0.04, and 0.06 *M* solutions, respectively, of Aliquat 336 thiocyanate plus 0.01 *M* *n*-octylamine, in contrast to extractions of 2, 6, and 10%, respectively, in the absence of the amine. Similar enhancements of extraction were obtained from sulfate, chloride, and nitrate media. In similar experiments with cobalt, no enhancements of extraction were observed, and the absorption spectra of the organic phases showed that the extracted complex was substantially unaffected by the presence of the free amine.

The dependence of nickel distribution upon the concentration of *n*-octylamine for extraction by Aliquat 336 thiocyanate from 0.1 *M* NH_4Br was found to be of second order (Fig. 14), which is consistent with the expected extraction stoichiometry for the alkylammonium thiocyanate–amine mixture:

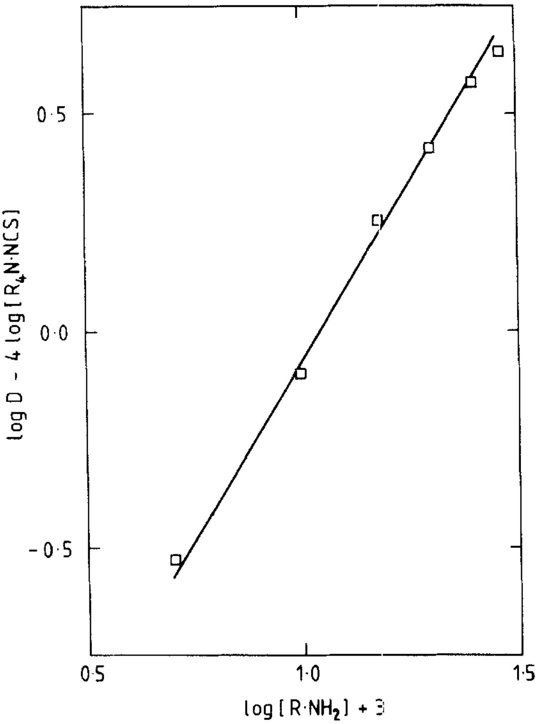

FIG. 14. Extraction of nickel(II) from 0.10 *M* NH_4Br by 0.04 *M* Aliquat 336 thiocyanate in the presence of *n*-octylamine in xylene.

$$Ni^{2+} + 2X^- + 4R_4N.NCS + 2R.NH_2 = (R_4N)_2Ni(NCS)_4(R.NH_2)_2 + 2R_4N.X \qquad (23)$$

Finally, the equilibrium constant for Eq. (22) was determined by addition of known amounts of *n*-octylamine to a xylene solution containing 0.0008 *M* nickel(II) extracted into 0.02 *M* Aliquat 336 thiocyanate. Spectrophotometric analysis of the solutions at 345 and 425 nm allowed the concentrations of the species involved to be evaluated; it was assumed that the organic phases contained sufficient dissolved water to render the activity of that species constant. The calculated values for the equilibrium constants using spectrophotometric data at 345 and 425 nm (Table 3) are seen to be relatively consistent, with a mean value of 0.33 ± 0.05.

CONCLUSIONS

The extent of extraction of cobalt(II) and nickel(II) by Aliquat 336 thiocyanate in xylene increases with increasing stability of the co-extracted ion-pair formed between the counteranion, initially present in the aqueous phase, and the quaternary ammonium cation.

Extraction of cobalt takes place according to the general equation

$$Co^{2+} + 2X^- + 4R_4N.NCS = (R_4N)_2Co(NCS)_4 + 2R_4N.X$$

in which the extracted cobalt complex contains an anion of tetrahedral symmetry.

TABLE 3

Concentration Equilibrium Constants for the Reaction

$$Ni(NCS)_4^{2-} + 2R.NH_2 = Ni(NCS)_4(R.NH_2)_2^{2-}$$

	Equilibrium constant using analysis at	
[R.NH$_2$], $M \times 10^3$	345 nm	425 nm
1.0	0.35	0.24
2.0	0.36	0.31
4.0	0.38	0.34
6.0	0.36	0.36
10.0	0.29	0.29

In the case of nickel, the extracted complex contains an anion of octahedral symmetry, probably $Ni(NCS)_4(H_2O)_2^{2-}$. The poor extractability of nickel appears to result from secondary aquation of this complex anion. The coordinated water molecules in the nickel complex can be replaced by *n*-octylamine, with consequent enhancement of the extraction.

Acknowledgment

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