Liquid–Liquid Extraction of Thiocyanate and Thiocyanatoferrate(III) Complexes with Tris(3,5,5-trimethylhexyl)amine

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The distribution ratio of iron(III) at initial concentration 10^{-4}M has been measured using aqueous solutions of potassium nitrate and thiocyanate, at pH 2, with ionic strengths 0·25 and 0·50M, and an organic phase of tris(3,5,5-trimethylhexyl)amine in benzene. Concentrations of thiocyanate and of the amine were varied. An extraction equation was derived and found to be in good agreement with the results up to a thiocyanate concentration of 0·025M. Values of extraction equilibrium constants were calculated in several ways.

LIQUID–LIQUID extraction is an operation whose importance in the hydrometallurgical separation of metals has increased considerably in recent years. Much empirical effort has been devoted to the development of suitable methods for separating metals by this technique, but it should be possible to predict such separations from a knowledge of aqueous phase stability constants and extraction equilibrium constants. A study was therefore made of the extraction of metal complexes in a system for which sufficient stability constant data were available [*i.e.* iron(III)–thiocyanate]. The extractant was the tertiary amine 'tri-isononylamine,' tris(3,5,5-trimethylhexyl)amine, which had been used in related studies [1,2] and at the start of the work was commercially available. Benzene was used as diluent to minimise any danger of formation of two organic phases. Aqueous phase activity coefficients were controlled by potassium nitrate as stability constants of the iron complexes had previously been measured in this medium [3] and for this reason the amine was converted to the nitrate form by pre-equilibration of the organic phase with dilute nitric acid.

Thus the extraction equilibria involved can be written as in equations (1) and (2). Equations similar to (2)

$$R_3NHNO_{3\,(org)} + SCN^-_{(aq)} \rightleftharpoons R_3NHSCN_{(org)} + NO_3{}^-_{(aq)} \qquad (1)$$

$$R_3NHSCN_{(org)} + Fe(SCN)_4{}^-_{(aq)} \rightleftharpoons R_3NHFe(SCN)_{4\,(org)} + SCN^-_{(aq)} \qquad (2)$$

but involving higher thiocyanatoferrate(III) species might also be required to explain the observed behaviour but their importance would depend on the relative values of β_4, β_5, and β_6.[3] From equations (1) and (2), equations, which relate the distribution coefficients of both SCN⁻ and iron to the respective equilibrium constants, can easily be derived. These are similar in form to empirical equations previously proposed for metal extraction systems by Lloyd and Oertel [4] and by Ellis.[5] This paper endeavours to obtain values for the extraction equilibrium constants of equations (1) and (2), and to show that both the equations derived from the equilibria and plots derived from the Lloyd equation [4] adequately represent the experimental data.

EXPERIMENTAL

Tris(3,5,5-trimethylhexyl)amine (I.C.I.) was fractionally distilled *in vacuo* and stored over sodium hydroxide pellets. The equivalent weight determined by titration was 399, (calc. 395·7). Solutions in A.R. grade benzene were used for extraction and were pre-equilibrated as follows. (i) When investigating the effects of changing thiocyanate concentration, each was shaken with an equal volume of thiocyanate-free electrolyte which was otherwise identical in composition and pH with that to be used in the subsequent extraction of thiocyanate or iron. (ii) In groups of experiments, in which the amine concentration was varied, pre-equilibration was carried out with solutions containing potassium thiocyanate at concentration equal to, and nitric acid at concentration 0·01M greater than, that of the amine; otherwise too much SCN^- was removed from the aqueous phase to permit the formation of anionic iron species. The concentrations of thiocyanate in the organic phase were calculated using equation (9), as were the equilibrium concentrations of thiocyanate in the two phases after extraction of iron.

Aqueous phases for investigating the extraction of thiocyanate were prepared from stock solutions of potassium nitrate and of potassium thiocyanate labelled with either ^{14}C or ^{35}S (Radiochemical Centre, Amersham); the pH was adjusted to 2 with nitric acid before equilibration. Aqueous solutions for studying the extraction of iron were prepared similarly using unlabelled thiocyanate and stock 10^{-3}M-ferric nitrate solution containing ^{59}Fe and 0·1M-nitric acid. Equal volumes of aqueous and organic phases were equilibrated by shaking together in separating funnels for 2 min at room temperature, 18—25 °C. Within this range a temperature change had no detectable effect on the results. When the distribution of thiocyanate was measured, single channel liquid scintillation counting was used at −23° (^{14}C) or −15° (^{35}S). In the case of the aqueous solutions, 0·5 ml of solution was added to ethanol (10 ml) and phosphor (10 ml) (8 g of PPO and 0·36 g of POPOP per l toluene). Iron concentrations were measured by gamma scintillation counting with a Tl/NaI phosphor. The background count of the aqueous phase was measured using a solution containing the appropriate concentration of potassium salt, to allow for the activity of ^{40}K. All counts were corrected for a scaler resolving time of 5 μs.

Nitrate concentrations in aqueous solutions were measured spectrophotometrically at 300 nm (Unicam SP 500). Beer's law was obeyed even in the presence of 0·05M-potassium thiocyanate. Solutions containing up to 0·25M-nitrate could be used without dilution and the accuracy of measurement of concentration was within 3—4% of that calculated from the mass balance. All extraction experiments were carried out in quadruplicate.

At aqueous thiocyanate concentrations above about

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[1] U. Bertocci, U.K. Atomic Energy Authority, No. AERE/R-2933, 1959.

[2] A. R. Burkin, 'Unit Processes in Hydrometallurgy,' Gordon and Breach, New York, 1964, p. 529.

[3] 'Stability Constants of Metal-Ion Complexes,' The Chemical Society, London, 1964.

[4] P. J. Lloyd and M. K. Oertel, 'Unit Processes in Hydrometallurgy,' Gordon and Breach, New York, 1964, p. 453.

[5] D. A. Ellis, *Ind. and Eng. Chem.*, 1960, **52**, 251.

0·025M at pH 2 and at all concentrations at pH 1 precipitation of yellow polymerised HSCN occurred in the organic phase. This interfered with counting and caused low values to be obtained for thiocyanate in this phase.

In order to minimise reduction of iron(III) by thiocyanate, extraction was carried out without delay after mixing the stock solution even though experiments carried out at different intervals after mixing showed that this precaution was not essential.

DISCUSSION AND RESULTS

Extraction of Thiocyanate.—The thermodynamic equilibrium constant of reaction (1) is given by equation (3). In organic solutions, amines and their salts have been shown to have activity coefficients which are practically independent of the anion, and are constant, particularly when the mole fraction present is less than 0·1.[6] With constant ionic strength in the aqueous phase, activity coefficients of ions may be assumed to be constant, particularly when one salt is present in a large excess.[7] Thus, for any group of experiments in which the ionic strength was kept at a single value, an equilibrium constant K'_{SCN} may be written using concentrations instead of activities.

$$K_{\mathrm{SCN}} = [\mathrm{R_3NHSCN}]_{\mathrm{org}}[\mathrm{NO_3^-}]_{\mathrm{aq}}/[\mathrm{R_3NHNO_3}]_{\mathrm{org}}[\mathrm{SCN^-}]_{\mathrm{aq}} \quad (3)$$

R_3NHSCN has a solubility below 6 p.p.m. ($1{\cdot}5 \times 10^{-5}$M) in the aqueous phase[8] or less than 0·1% of the total (*i.e.* well within experimental error) and polymerization of thiocyanate, as indicated by the formation of a yellow precipitate, was not observed at pH 2 below 0·025M total SCN^-. Hence the aqueous phase concentration of thiocyanate can be represented by $[\mathrm{SCN^-}]_{\mathrm{aq}}$. Organic phase polymerization of R_3NHSCN is unlikely to be significant (an assumption which will be justified) so that the distribution coefficient of thiocyanate is given by equation (4),

$$D_{\mathrm{SCN}} = [\mathrm{R_3NHSCN}]_{\mathrm{org}}/[\mathrm{SCN^-}]_{\mathrm{aq}}$$

$$\text{so that}\quad K'_{\mathrm{SCN}} = D_{\mathrm{SCN}}[\mathrm{NO_3^-}]_{\mathrm{aq}}/[\mathrm{R_3HNO_3}]_{\mathrm{org}}$$

$$\text{whence}\quad D_{\mathrm{SCN}} = K'_{\mathrm{SCN}}\{[\Sigma\mathrm{R_3N}]_{\mathrm{org}} - [\mathrm{R_3NHSCN}]_{\mathrm{org}}\}/[\mathrm{NO_3^-}]_{\mathrm{aq}} \quad (4)$$

where $[\Sigma\mathrm{R_3N}]_{\mathrm{org}}$ represents the sum of the concentrations of all the amine-containing species present in the organic phase, that is, the concentration of amine used when preparing the benzene solution.

Variation of D*SCN with Thiocyanate Concentration.*—In Figure 1, are given the experimental data on the change in D_{SCN} with aqueous thiocyanate concentration at equilibrium. The amine concentration was 0·01M and results are shown for three ionic strengths, 0·25, 0·50, and 0·75M. Each point is the mean of four extractions. The curves drawn were computed using the values of K'_{SCN} derived below.

In Figure 2, are given the experimental data on the change in D_{SCN} with equilibrium concentration of thiocyanate in the organic phase, under the same conditions of amine concentration and ionic strength. The straight lines drawn are the best fitting lines calculated by the method of least squares. Correlation coefficients are −0·950, −0·956, and −0·999 for ionic strengths 0·25, 0·50, and 0·75M, respectively.

It may be argued that when the amine thiocyanate salt is formed in the organic phase, it might be associated, or 'solvated,' in some way with the nitrate salt. The product could be written $\mathrm{R_3NHSCN},\nu\,\mathrm{R_3NHNO_3}$ and equation (1) altered accordingly. Since D_{SCN} varies linearly with $[\mathrm{R_3NHSCN}]_{\mathrm{org}}$, the values of ν must be zero, and the assumption that the activity coefficient of the amine salts is constant, is not invalidated.

The concentration of thiocyanate in the aqueous phase was less than 1% of the nitrate concentration in that phase, so that the value of $[\mathrm{NO_3^-}]_{\mathrm{aq}}$ in equation (4) may be taken to be the value of the ionic strength. The values of the slopes of the lines in Figure 2, and intercepts where $[\mathrm{R_3NHSCN}]_{\mathrm{org}}$ are given in Table 1a, together with the corresponding values of K'_{SCN}.

TABLE 1

(a)

I	Slope	K'_{SCN}	Intercept $[\mathrm{R_3NHSCN}]_{\mathrm{org}} = 0$	K'_{SCN}
0·25	−98·1	24·5	1·04	25·9
0·50	−57·7	28·8	0·578	28·9
0·75	−35·0	26·2	0·364	27·3

(b)

I	Slope	K'_{SCN}	Intercept $1/[\mathrm{R_3NHSCN}]_{\mathrm{org}} = 0$
0·25	105·4	26·3	−102·2
0·50	54·9	27·5	−54·5
0·75	37·1	27·8	−37·3

I	Slope	K'_{SCN}	Intercept $1/[\mathrm{SCN}]_{\mathrm{aq}} = 0$	$[\Sigma\mathrm{R_3N}]_{\mathrm{org}}$
0·25	105·4	25·6	97·0	0·0103
0·50	54·9	27·3	99·3	0·0101
0·75	37·1	28·0	100·5	0·00995

The experimental information presented in Figures 1 and 2 may be analysed quantitatively in an alternative manner to check the validity of describing the extraction behaviour in terms of equation (4) which may be arranged in the form of equation (5). The data contained in Figures 1 and 2 are shown in Figure 3 plotted as $1/[\mathrm{R_3NHSCN}]_{\mathrm{org}}$ against $1/[\mathrm{SCN^-}]_{\mathrm{aq}}$, the lines being calculated by the method of least squares. Correlation coefficients were 0·998, 0·999, and 0·998 for ionic strengths 0·25, 0·50, and 0·75M, respectively. The values of slopes and intercepts, together with the corresponding values of K'_{SCN}, are given in Table 1b. The amine concentration used was 0·01M, and the interception of the lines on the $1/[\mathrm{SCN^-}]_{\mathrm{aq}} = 0$ axis gives a value in good agreement with this.

$$\frac{1}{[\mathrm{R_3NHSCN}]_{\mathrm{org}}} = \frac{[\mathrm{NO_3^-}]_{\mathrm{aq}}}{K'_{\mathrm{SCN}}[\Sigma\mathrm{R_3N}]_{\mathrm{org}}}\,\frac{1}{[\mathrm{SCN^-}]_{\mathrm{aq}}} + \frac{1}{[\Sigma\mathrm{R_3N}]_{\mathrm{org}}} \quad (5)$$

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[6] A. S. Kertes, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1764; 1965, **27**, 209.

[7] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 3rd edn., 1958.

[8] M. W. Desai and T. K. S. Murthy, *Analyst*, 1963, **88**, 322.

This method of plotting reciprocal concentrations in the two phases, based on equation (5), is equivalent to the method used by Lloyd and Oertel [4] who considered the variation of free amine concentration with the concentration of metal in the organic phase, and aggregation of the amine.

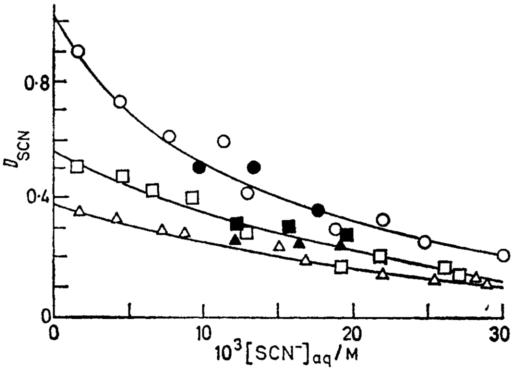

FIGURE 1 Dependence of D_{SCN} on aqueous thiocyanate concentration at equilibrium for ionic strengths 0·25 (○), 0·50 (□), and 0·75M (△). Amine concentration 0·01M. Filled points determined using thiocyanate labelled with ^{35}S, open points with ^{14}C. Curves calculated from K'_{SCN} values using equation (4)

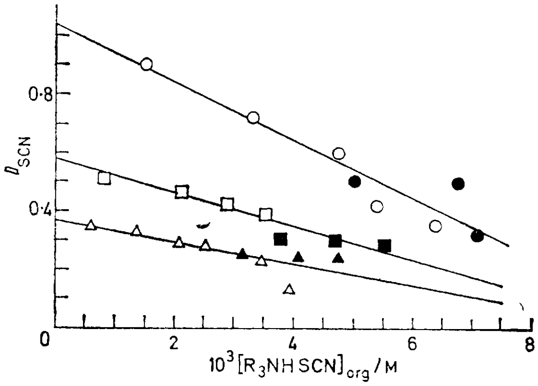

FIGURE 2 Dependence of D_{SCN} on equilibrium organic thiocyanate concentration, conditions as in Figure 1

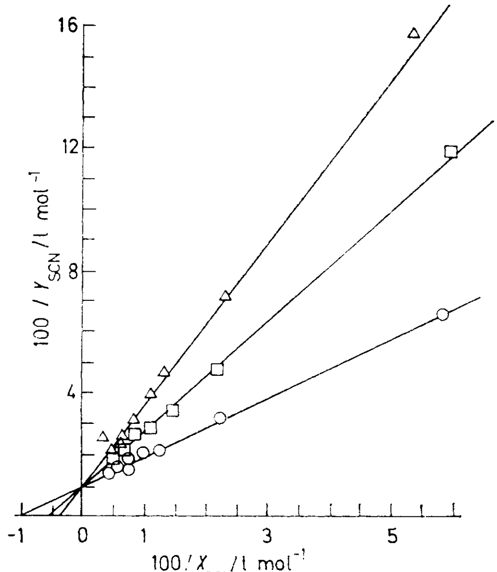

FIGURE 3 Reciprocal diagram for thiocyanate extraction, conditions as in Figure 1

The mean values of K_{SCN} obtained by combining the results of all the methods of calculation were:

Ionic strength	0·25	0·50	0·75
K'_{SCN}	25·6 ± 0·7	28·1 ± 0·8	27·3 ± 0·7

These values were used in equation (4) to calculate the curves drawn through the experimental points in Figure 1. The variation of K'_{SCN} with ionic strength is probably due in part to statistical errors and partly to the assumption that $[SCN^-]_{aq}$ is negligibly small compared with $[NO_3^-]_{aq}$, which will give a smaller error at higher ionic strengths. If it is assumed that K'_{SCN} is independent of ionic strength, the mean value is **27·0 ± 1·3**.

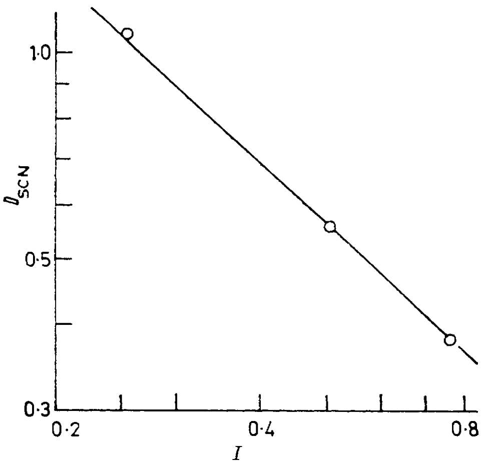

FIGURE 4 Dependence of D_{SCN} on ionic strength, logarithmic plot

Variation of D_{SCN} with Ionic Strength.—Equation (4) may be rearranged as in equation (6), putting $[NO_3^-]_{aq}$ equal to the ionic strength, I, which yields equation (6′).

$$D_{SCN} = K_{SCN}[\Sigma R_3N]/\{I + [SCN^-]_{aq}(K_{SCN})^{-1}\} \quad (6)$$

$$\frac{\partial \log D_{SCN}}{\partial \log I} = -\frac{I}{I + (K_{SCN})^{-1}}[SCN]^-_{aq} \quad (6')$$

Thus, when $[SCN^-]_{aq} = 0$, $\partial \log D_{SCN}/\partial \log I = -1$. The appropriate values of D_{SCN} extrapolated in Figure 1 are plotted logarithmically in Figure 4; the slope of the line drawn is —0·95. Strictly, activities of SCN^- and not concentrations must be used under conditions of varying ionic strength, but when $[SCN^-]_{aq} = 0$, this term cancels out so that, at zero $[SCN^-]_{aq}$ the slope is correct.

Variation of D_{SCN} with Amine Concentration.—The experimental results are given in Figure 5; the straight line drawn has slope 1·19. When $[SCN^-]_{aq}$ and I are constant, equation (6) gives:

$$\partial \log D_{SCN}/\partial \log [\Sigma R_3N]_{org} = 1$$

However, in the experiments $[SCN^-]_{aq}$ was not kept constant so that the total derivative must be considered, *i.e.* equation (7).

$$\frac{\mathrm{d}\log D_{\mathrm{SCN}}}{\mathrm{d}\log[\Sigma R_3N]_{\mathrm{org}}} = \frac{\partial\log D_{\mathrm{SCN}}}{\partial\log[\Sigma R_3N]_{\mathrm{org}}} + \frac{\partial\log D_{\mathrm{SCN}}}{\partial\log[\mathrm{SCN}^-]_{\mathrm{aq}}}\cdot\frac{\mathrm{d}\log[\mathrm{SCN}^-]_{\mathrm{aq}}}{\mathrm{d}\log\Sigma[R_3N]_{\mathrm{org}}} = 1 + \Delta \quad (7)$$

where

$$\Delta = -\frac{[\mathrm{SCN}^-]_{\mathrm{aq}}(K'_{\mathrm{SCN}} - 1)}{I + (K'_{\mathrm{SCN}} - 1)[\mathrm{SCN}^-]_{\mathrm{aq}}}\cdot\frac{\mathrm{d}\log[\mathrm{SCN}^-]_{\mathrm{aq}}}{\mathrm{d}\log[\Sigma R_3N]_{\mathrm{org}}} = (-a)b$$

The term $(-a)$ is always negative and is small in value when $[\mathrm{SCN}^-]_{\mathrm{aq}}$ is small compared to 1. It increases as $[\mathrm{SCN}^-]_{\mathrm{aq}}$ increases. Also, $[\mathrm{SCN}^-]_{\mathrm{aq}}$ decreases as $[\Sigma R_3N]_{\mathrm{org}}$ increases, because of the rise in value of D_{SCN}. The rate of this decrease is more rapid at higher values of $[\Sigma R_3N]_{\mathrm{org}}$. Thus, the term Δ will be positive and increase as the total amine concentration increases.

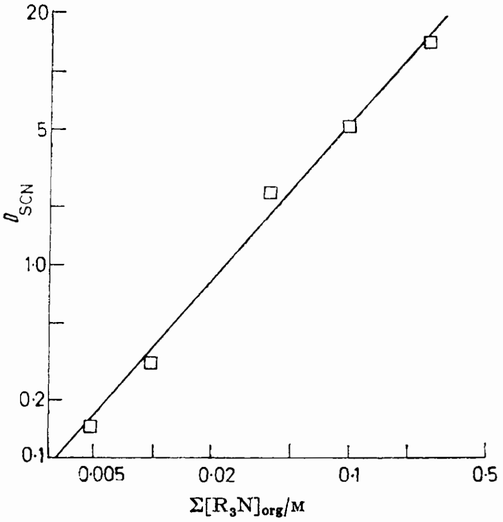

FIGURE 5 Dependence of D_{SCN} on amine concentration, logarithmic plot

Calculations showed that when $[\Sigma R_3N]_{\mathrm{org}} = 0{\cdot}005$M, $\Delta = 0{\cdot}01$, and when $[\Sigma R_3N]_{\mathrm{org}} = 0{\cdot}25$M, $\Delta = 0{\cdot}5$. The slope of the line drawn in Figure 5 is, therefore, within the range expected.

Extraction of Iron.—The formation of a compound between iron(III) thiocyanate complexes and small amounts of long-chain aliphatic amines in aqueous solution has been used to determine the concentration of the amine.[8] The salt was extracted into cyclohexane and the intensity of the absorption peak at 490 nm measured. The extraction of the tributylamine complex $(R_3NH)_3Fe(SCN)_6$ from solutions of ferric chloride and ammonium thiocyanate at pH 3·4 has been reported.[9] The compound has an absorption peak at 515 nm in amyl acetate. It has recently been reported[10] that when iron(III) thiocyanate complexes are extracted by tri-n-octylamine thiocyanate solutions of different concentrations, using several diluents, the value of $\partial\log D_{\mathrm{Fe}}/\partial\log[R_3NHSCN]_{\mathrm{org}}$ was 2 in each case. It was concluded that the predominant aqueous species extracted was $Fe(SCN)_5^{2-}$. It has been shown[11] that in solutions containing iron at concentrations less than 0·025M the extraction equilibrium is

$$R_3NHSCN_{(\mathrm{org})} + Fe(SCN)_4{}^-{}_{(\mathrm{aq})} \rightleftharpoons R_3NHFe(SCN)_{4(\mathrm{org})} + SCN^-{}_{(\mathrm{aq})}$$

and the extraction equation may be written as in equation (8).

$$D_{\mathrm{Fe}} = K_{\mathrm{ex}(4)}\,\alpha_4([R_3NHSCN]_{\mathrm{org}} - [\mathrm{Fe}]_{\mathrm{org}})/[\mathrm{SCN}^-]_{\mathrm{aq}} \quad (8)$$

Here, $D_{\mathrm{Fe}} = [\mathrm{Fe}]_{\mathrm{org}}/[\mathrm{Fe}]_{\mathrm{aq}}$, no account being taken of the species in which the iron occurs; $K_{\mathrm{ex}(4)}$ is the equilibrium constant for the extraction equation involving $Fe(SCN)_n{}^{(n-3)-}$, in the case where $n = 4$, expressed in terms of concentrations; α_4 is the fraction of the iron in the aqueous phase which is present as $Fe(SCN)_4{}^-$. $[\mathrm{Fe}]_{\mathrm{org}}$ is the concentration of iron found by experiment to be in the organic phase. It was found that the value of D_{Fe} varied systematically with iron concentration in the range 2×10^{-5} to 2×10^{-4}M and that this variation could be explained by postulating the formation of the polymeric species $Fe_2(SCN)_6$ in the aqueous phase. Values of the stability constant β_{62} for this species were calculated to be $(0{\cdot}52 \pm 0{\cdot}13) \times 10^{16}$ and $(0{\cdot}33 \pm 0{\cdot}13) \times 10^{16}$ at ionic strengths 0·25 and 0·50M, respectively. From these figures and the published stability constant data for the complexes of iron(III) with nitrate,[12] hydroxide,[13-15], and thiocyanate,[16] as ligands, values of α_4 and hence of $K_{\mathrm{ex}(4)}$ were calculated; the values of $K_{\mathrm{ex}(4)}$ were $5{\cdot}26 + 0{\cdot}12$ and $9{\cdot}50 + 0{\cdot}02$ at ionic strengths 0·25 and 0·50M respectively. Results were not reported for ionic strength 0·75M because the experiments on which these were based were carried out about 2 years after those at the two lower ionic strengths. During this period of storage, the amine had apparently decomposed to some extent.

Since it was shown above that extraction of thiocyanate by the amine can be represented sufficiently quantitatively by equation (4), with $K'_{\mathrm{SCN}} = 27{\cdot}0$, the values of $[R_3NHSCN]_{\mathrm{org}}$ can be calculated for any set of experimental conditions. This is most conveniently done in terms of known concentrations by writing $D_{\mathrm{SCN}} = R_3NHSCN_{\mathrm{org}}/(c_{\mathrm{SCN}} - [R_3NHSCN]_{\mathrm{org}})$, where c_{SCN} is the total concentration of thiocyanate in both phases (that is the concentration present in the aqueous solution initially) and rearranging equation (4) as equation (9),

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[10] H. Watanabe and M. Murozumi, *Bull. Chem. Soc., Japan*, 1967, **40**, 1006.

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[13] K. Schlyter, *Trans. Roy. Inst. Technol. Stockholm*, 1962, Nr. 195 and 196.

[14] G. Biederman, cited in ref. 13.

[15] R. M. Milburn and W. C. Vosburgh, *J. Amer. Chem. Soc.*, 1955, **77**, 1352; 1957, **79**, 537.

[16] V. E. Mironov and Y. I. Rutkovskii, *Zhur. neorg. Khim.*, 1965, **10**, 1069.

where, now, the ionic strength $I = [NO_3^-]_{aq} + [SCN^-]_{aq}$.

$$K'_{SCN} = [R_3NHSCN]_{org}(I - c_{SCN} + [R_3NHSCN]_{org}) / (c_{SCN} - [R_3NHSCN]_{org})([\Sigma R_3N]_{org} - [R_3NHSCN]_{org}) \quad (9)$$

Variation of D_{Fe} with Thiocyanate Concentration.—With iron concentration 10^{-4}M, when the thiocyanate concentration is less than 0·025M the only anionic, and so extractable, iron species present in significant quantity is $Fe(SCN)_4^-$. These concentration ranges, therefore, provide the simplest conditions under which to try to account for the change in D_{Fe} with change in thiocyanate concentration, in terms of the stability constants for the complexes of iron(III) with all of the anions present in the solution; thiocyanate, nitrate, and hydroxide. Experimental results for the change in D_{Fe} are shown in Figure 6.

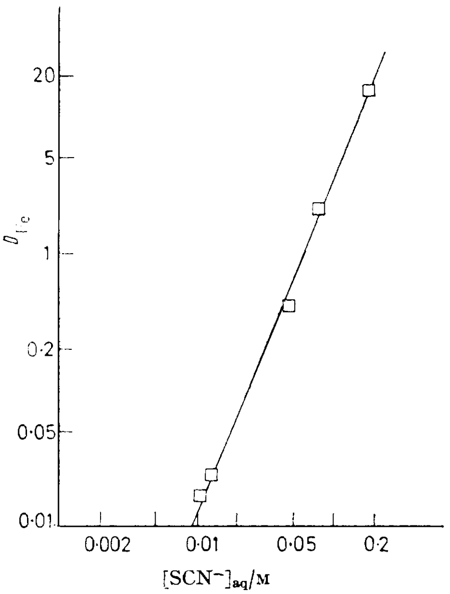

FIGURE 6 Dependence of D_{Fe} on aqueous thiocyanate concentration, logarithmic plot

If $[Fe]_{org}$ is negligible in comparison with $[R_3NHSCN]_{org}$, then the extraction equation (8) can be rearranged to give equation (8′) since, $\alpha_4 = \beta_4[Fe^{3+}]_{aq}[SCN^-]_{aq}^4/[\Sigma Fe]_{aq}$, the fraction of iron present as uncomplexed Fe^{3+} ions being written α_0.

$$\log D_{Fe} = \log K_{ex(4)} + \log \beta_4 + 3 \log [SCN^-]_{aq} + \log [R_3NHSCN]_{org} + \log \alpha_0 \quad (8')$$

The assumption is made that all of the thiocyanate determined experimentally in the aqueous phase is present as uncomplexed ions, *i.e.* $[Fe]_{aq}$ is negligible in comparison with $[SCN^-]_{aq}$. The overall stability constant for the ion $Fe(SCN)_4^-$ is written β_4.

Differentiation of this equation with respect to log $[SCN^-]_{aq}$ gives equation (10).

$$\frac{d \log D_{Fe}}{d \log [SCN^-]_{aq}} = 3 + \frac{d \log \alpha_0}{d \log [SCN^-]_{aq}} + \frac{d \log [R_3NHSCN]_{org}}{d \log [SCN^-]_{aq}} \quad (10)$$

The distribution of thiocyanate with changing total concentration has been determined experimentally, and to obtain the final term, it is necessary only to use the appropriate form of the extraction equation. Prediction of the way D_{Fe} will change with changing thiocyanate concentration requires, therefore, a knowledge of d log α_0/d log $[SCN^-]_{aq}$. At constant ionic strength, and nearly constant concentrations of nitrate and hydroxide ions, a change in thiocyanate concentration will affect α_0 by altering the concentrations of the various thiocyanatoferrate(III) species including the polymeric species $Fe_2(SCN)_6$. In the solutions used α_0 is given by the equation

$$\alpha_0 = \frac{1}{1 + \sum_1^2 {}^*\beta_n[H^+]^{-n} + K_{NO_3}[NO_3^-]_{aq} + \sum_1^6 \beta_n[SCN^-]_{aq}^n + 2\beta_{62}\alpha_0[SCN^-]_{aq}^6[Fe]_{aq}}$$

where K_{NO_3} is the stability constant for the first iron(III) nitrate complex and ${}^*\beta_n$ refers to the formation of hydroxo-species in terms of $[H^+]$. Implicit differentiation gives:

$$\frac{d\alpha_0}{d[SCN^-]_{aq}} = -\frac{\alpha_0(\sum_1^6 n\beta_n[SCN^-]_{aq}^{n-1} + 12\beta_{62}\alpha_0[SCN^-]_{aq}^5[Fe_{aq}])}{1 + \sum_1^2 {}^*\beta_n[H^+]^{-n} + K_{NO_3}[NO_3^-]_{aq} + \sum_1^6 \beta_n[SCN^-]_{aq}^n + 4\beta_{62}\alpha_0[SCN^-]_{aq}^6[Fe]_{aq}}$$

From this, it can be shown that

$$\frac{d \log \alpha_0}{d \log [SCN^-]_{aq}} = -\frac{\sum_1^6 n\alpha_n + 6\alpha_{62}}{1 + \alpha_{62}}$$

where α_{62} is the fraction of the iron present in the aqueous phase as $Fe_2(SCN)_6$. Since the thiocyanate extraction equation (4) yields equation (4′), then equation (9) becomes equation (11).

$$\frac{d \log [R_3NHSCN]_{org}}{d \log [SCN^-]_{aq}} = \frac{[\Sigma R_3N]_{org} - [R_3NHSCN]_{org}}{[\Sigma R_3N]_{org}} \quad (4')$$

$$\frac{d \log D_{Fe}}{d \log [SCN^-]_{aq}} = 3 + \frac{[\Sigma R_3N]_{org} - [R_3NHSCN]_{org}}{[\Sigma R_3N]_{org}} - \frac{\sum_1^6 n_n + 6\alpha_{62}}{1 + \alpha_{62}} \quad (11)$$

The stability constants used in calculations have been listed[11] and the values relevant to the ionic strengths used in experiments were calculated using equation (a),

$$\log K_n = \log K_n^0 + [A\Delta ZI^{\frac{1}{2}}/(1 + BI^{\frac{1}{2}})] + CI \quad (a)$$

where $A = 0{\cdot}509$ and the values of the other parameters used have been given previously.[11]

With initial iron concentration 10^{-4}M and thiocyanate concentrations in the range (1·5—2·5) × 10^{-2}M the species $Fe(SCN)_5^{2-}$ and $Fe(SCN)_6^{3-}$ are formed to a very small extent, α_5 and α_6 being less than 10^{-4}. Hence, the only extractable species which needs to be considered is $Fe(SCN)_4^-$ and $D_{Fe} = \alpha_4 P_4$ where P_4 is the partition coefficient for that ion ($P_4 = [Fe(SCN)_4^-]_{org}/[Fe(SCN)_4^-]_{aq}$); equation (**12**) is thus obtained

$$K_{ex(4)} = \frac{[Fe]_{org}}{[Fe(SCN)_4^-]_{aq}} \frac{[SCN^-]_{aq}}{[R_3NHSCN]_{org}} = \frac{P_4}{D_{SCN}} = \frac{D_{Fe}}{\alpha_4 D_{SCN}} \qquad (12)$$

Experimental and derived data are given in Table **2**. The mean values of $K_{ex(4)}$, $5{\cdot}1 \pm 0{\cdot}12$ and $8{\cdot}7 \pm 0{\cdot}7$ at ionic strengths 0·25 and 0·50M, agree reasonably well with those reported previously,[11] $5{\cdot}3 \pm 0{\cdot}1$ and $9{\cdot}5 \pm 0{\cdot}1$.

TABLE 2

Distribution ratios and extraction constants of iron(III) at $[\Sigma R_3N]_{org} = 0{\cdot}01$M; $c_{Fe} = 1{\cdot}009 \times 10^{-4}$M

I	c_{SCN} 10^2M	$[SCN^-]_{aq}$ 10^3M	D_{Fe} $\times 10^2$	α_{62} $\times 10^2$	α_4 $\times 10^2$	P_4	D_{SCN}	$K_{ex(4)}$
0·25	1·5	9·87	1·93	4·01	0·77	2·50	0·519	4·82
	2·0	14·3	4·53	14·8	2·15	2·11	0·403	5·23
	2·5	18·3	8·38	20·7	4·43	1·89	0·364	5·18
Mean $K_{ex(4)} = 5{\cdot}1 \pm 0{\cdot}2$								
0·50	1·5	11·1	1·71	4·60	0·59	2·89	0·351	8·22
	2·0	15·3	3·92	15·8	1·52	2·85	0·307	8·40
	2·0	15·3	3·78	15·2	1·52	2·49	0·307	8·08
	2·5	19·6	7·38	26·3	2·86	2·58	0·272	9·49
	2·5	19·6	6·98	30·6	2·70	2·58	0·272	9·48
Mean $K_{ex(4)} = 8{\cdot}7 \pm 0{\cdot}7$								

TABLE 3

Calculated values of d log D_{Fe}/d log $[SCN^-]_{aq}$ at constant amine concentration

Ionic strength	Initial $[SCN^-]_{aq}$ 10^2M	$\frac{\Sigma n\alpha_n + 6\alpha_{62}}{1 + \alpha_{62}}$	$\frac{[\Sigma R_3N]_{org} - [R_3NHSCN]_{org}}{[\Sigma R_3N]_{org}}$	$\frac{d \log D_{Fe}}{d \log [SCN^-]_{aq}}$
0·25	1·5	0·90	0·49	2·58
	2·0	1·57	0·43	1·86
	2·5	1·94	0·33	1·39
0·50	1·5	0·78	0·60	2·82
	2·0	1·41	0·53	2·12
	2·0	1·41	0·53	2·12
	2·5	1·89	0·47	1·58
	2·5	1·99	0·47	1·47

Calculated values of the slope are given in Table 3. Equation (11) indicates log D_{Fe} should not vary linearly with log $[SCN^-]_{aq}$. The linearity shown in Figure 6 is, therefore, due to the restricted concentration range and experimental statistical errors.

Variation of D_{Fe} *with Amine Concentration.*—It was found that when the amine solution was pre-equilibrated with nitric acid only, D_{Fe} fell with increasing amine concentration, because the larger amounts of amine extracted increasing quantities of thiocyanate, leaving less in the aqueous phase to form an extractable thiocyanatoferrate(III). For this reason, the amine was pre-equilibrated with solutions containing both nitrate and thiocyanate, and the final value of $[SCN^-]_{aq}$ was calculated using equation (9). Experimental and calculated data are given in Table 4. With amine concentrations of 0·05M and above, the aqueous thiocyanate concentrations were large enough to cause significant fractions of the iron to be present as $Fe(SCN)_5^{2-}$ and $Fe(SCN)_6^{3-}$. Exchange reactions of these ions with $[R_3NHSCN]_{org}$ with extraction equilibrium constants $K_{ex(5)}$ and $K_{ex(5)}$ respectively must be considered.

TABLE 4

Variation of D_{Fe} with amine concentration and calculated thiocyanate concentrations ($I = 0{\cdot}50$M)

$c_{Fe} = 0{\cdot}954 \times 10^{-4}$M

Pre-equilibration

	Initial	Initial	Calculated by (4)	
$[\Sigma R_3N]_{org}$ M	$[HNO_3]_{aq}$ M	$[SCN^-]_{aq}$ M	$[R_3NHSCN]_{org}$ M	$[SCN^-]_{aq}$ M
0·005	0·01			
0·010	0·01			
0·050	0·06	0·05	0·0384	0·0116
0·10	0·11	0·10	0·0773	0·0227
0·25	0·26	0·25	0·204	0·0462

Equilibration with ferric thiocyanate ($c_{SCN} = 0{\cdot}015$M)

$[\Sigma R_3N]_{org}$ M	$[SCN^-]_{aq}$ M	$[R_3NHSCN]_{org}$ M	D_{SCN} (calculated)	D_{Fe} (measured)
0·005	0·0130	0·00184	0·142	0·0232
0·010	0·0111	0·0039	0·311	0·0171
0·050	0·0451	0·00835	0·185	0·414
0·10	0·0740	0·0183	0·247	2·12
0·25	0·177	0·0418	0·236	15·3

The distribution coefficient of iron with three extractable species present will be determined by the individual partition coefficient of each and the fraction of the total amount of iron present as each extractable species, equation (b). From equation (12) and the definitions of $K_{ex(5)}$ and $K_{ex(6)}$ this becomes equation (c),

$$D_{Fe} = \alpha_4 P_4 + \alpha_5 P_5 + \alpha_6 P_6 \qquad (b)$$

$$D_{Fe} = \alpha_4 K_{ex(4)} D_{SCN} + \alpha_5 K_{ex(5)} D^2{}_{SCN} + \alpha_6 K_{ex(6)} D^3{}_{SCN} \qquad (c)$$

and since $\alpha_n = \beta_n[Fe^{3+}][SCN^-]^n/[Fe]_{aq} = \alpha_0\beta_n[SCN^-]_{aq}{}^n$ we obtain equation (13).

$$D_{Fe} = \alpha_0[SCN^-]_{aq}{}^3(\beta_4 K_{ex(4)}[R_3NHSCN]_{org} + \beta_5 K_{ex(5)}[R_3NHSCN]_{org}{}^2 + \beta_6 K_{ex(6)}[R_3NHSCN]_{org}{}^3) \qquad (13)$$

The variation of log D_{Fe} with log $[R_3NHSCN]_{org}$ and with log $[SCN^-]_{aq}$ is given by the equations (14) and (15), similar in form to equation (11).

$$\frac{d \log D_{Fe}}{d \log [R_3NHSCN]_{org}} = \left\{3 - \frac{\sum_1^6 n\alpha_n + 6}{1 + \alpha_{62}}\right\} \frac{[\Sigma R_3N]_{org}}{[\Sigma R_3N]_{org} - [R_3NHSCN]_{org}} + \frac{\sum_4^6 (n - 3)\beta_n K_{ex(n)}[R_3NHSCN]_{org}{}^{(n-3)}}{\sum_4^6 \beta_n K_{ex(n)}[R_3NHSCN]_{org}} \qquad (14)$$

$$\frac{d \log D_{Fe}}{d \log [SCN^-]_{aq}} = \left\{\frac{\sum_4^6 (n - 3)_n K_{ex(n)}[R_3NHSCN]_{org}{}^{n-3}}{\sum_4^6 \beta_n K_{ex(n)}[R_3NHSCN]_{org}{}^{(n-3)}}\right\} \frac{[\Sigma R_3N]_{org}}{[\Sigma R_3N]_{org} - [R_3NHSCN]_{org}} + 3 - \frac{\sum_1^6 n\alpha_n + 6\alpha_{62}}{1 + \alpha_{62}} \qquad (15)$$

Values of $K_{ex(n)}$ can be obtained by solving equation (13) simultaneously for three values of $[SCN^-]_{aq}$, and those for ionic strength 0·50M are given in Table 5.

TABLE 5

Calculation of $K_{ex(4)}$, $K_{ex(5)}$, and $K_{ex(6)}$, ionic strength 0·50M

$[\Sigma R_3N]_{org}$ (M)	0·05	0·10	0·25
$10^2[SCN^-]_{aq}$ (M)	4·506	7·404	17·70
$10^2[R_3NHSCN]_{org}$ (M)	0·835	1·827	4·180
D_{Fe}	0·414	2·11	15·33
D_{SCN}	0·185	0·247	0·236
α_4	0·103	0·231	0·606
α_5	0·003	0·010	0·066
α_6	5×10^{-5}	3×10^{-4}	0·005
$K_{ex(4)}$		15·4	
$K_{ex(5)}$		$6·6 \times 10^2$	
$K_{ex(6)}$		$1·6 \times 10^5$	

When $\log D_{Fe}$ was plotted against $\log [SCN^-]_{aq}$, $\log D_{Fe}$ against $\log [R_3NHSCN]_{org}$, and $\log D_{Fe}$ against $[\Sigma R_3N]_{org}$, using all of the data given in Tables 2, 4, and 5, reasonable straight lines were obtained by the method of least squares. The values of the slopes of these lines are compared in Table 6 with the values calculated using equations (14) and (15). Tolerable agreement was shown when $\log [R_3NHSCN]_{org}$ data were used, but agreement was poor when $\log [SCN^-]_{aq}$ was considered. One reason for this is probably the inaccuracy of the calculated values of $[SCN^-]_{aq}$, which arises from the formation of polymeric thiocyanic acid in the solutions used for pre-equilibration. These solutions contained relatively high concentrations of thiocyanate and nitric acid and formation of a yellow precipitate could be observed.

It is clear that even when considering a relatively simple system, for which most of the necessary data are available, calculation of the effects of varying the concentrations of the chemical substances, on the distribution coefficient of a metal, is difficult. However, a knowledge of the values of extraction constants, K_{ex}, for important systems would be of considerable use.

TABLE 6

Comparison of calculated and measured slopes for varying amine concentration (ionic strength 0·50M)

$[\Sigma R_3N]_{org}$ (M)	0·05	0·10	0·25	Mean
$d \log D_{Fe}/d \log [R_3NHSCN]_{org}$	1·60	2·08	1·81	1·9
Measured slope		2·5		
$d \log D_{Fe}/d \log [SCN^-]_{aq}$	1·36	1·72	1·38	1·5
Measured slope		2·3		

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