Solvent Extraction from Halide Solutions. Part VI.[†] Complexing Constants for Ferric Thiocyanates and the Temperature Dependence of Their Extraction

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Analysis of data on the solvent extraction of iron from thiocyanate solutions by trioctylphosphine oxide in carbon tetrachloride gives for the logarithms of the successive stability constants for the species $Fe(SCN)_n^{3-n}$ (n = 1—6): 2·09, 1·48, 1·00, 0·67, 0·18, and −0·6 at 20 °C and in an aqueous phase 0·2M in acid and 2M in total perchlorate. Succession constants are assumed to be related by $K_n/K_{n+1} = n(6 - n)/(6 - n + 1)(n + 1)k$. The partition coefficient for the extracting $Fe(SCN)_3$ is 52·3 with a $2{\cdot}2 \times 10^{-5}$M-phosphine oxide solution. Partition coefficients are also obtained for $Fe(SCN)_3$ and $Fe(SCN)_4^-$ with solutions of butyl dibutylphosphinate, dibutyl butylphosphonate, and tributyl phosphate in carbon tetrachloride. The temperature-dependence of the extraction has been measured and an attempt is made to interpret the data in terms of the various enthalpy changes involved. Comparative data on the extraction of ferric chloride and bromide have been obtained and the differences between extraction in the thiocyanate and halide systems discussed.

The Stability Constants.—Solvent extraction data are frequently used to determine stability constants and of the five [1-5] sets of successive constants for the complexing of ferric ion by thiocyanate so far reported, two [2,5] are dependent on such data. In the first such investigation [2] the authors used dimethyl ether as solvent and extracted from 0·18M-acid thiocyanate solutions. Molecular weight studies on the ethereal extract had suggested [6] that the extracting species was a solvate of the neutral $Fe(CNS)_3$. The stability

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[†] Part V, Z. Maksîmovič and A. G. Maddock, *J. Chem. Soc.* (*A*), 1971, 650.

[1] A. K. Babko, *Zhur. obshchei Khim.*, 1946, **16**, 1549; *Doklady Akad. Nauk S.S.S.R.*, 1946, **52**, 37.

[2] J. Y. Macdonald, K. M. Mitchell, and A. T. S. Mitchell, *J. Chem. Soc.*, 1951, 1574.

[3] E. Józefowicz and J. Maslowska, in Proc. Wroclaw Conf., 1962, ed. B. Jezowska-Trzebiatowska, Pergamon, Oxford, 1964, p. 530.

[4] V. P. Vasil'ev and P. S. Mukhina, *Zhur. neorg. Khim.*, 1964, **9**, 1134.

[5] V. E. Kironov and Yu. I. Rutkovskii, *Zhur. neorg. Khim.*, 1965, **10**, 1069.

[6] K. M. Mitchell and J. Y. Macdonald, *J. Chem. Soc.*, 1951, 1310.

constants were calculated on the assumption that only this species is extracted. The accuracy with which the third and fourth constants were evaluated was rather unsatisfactory. In a more recent investigation,[5] with use of the same solvent and a similar acidity of the aqueous phase, analysis of the organic phase suggested that an ion pair was extracted, which contained a, possibly solvated, $Fe(CNS)_4^-$ ion. Stability constants were calculated on the basis of the extraction of this species. Perhaps not unexpectedly the agreement between the two sets of results was not very good, the differences being especially marked for K_n with $n > 2$.

The results obtained in a previous Part[7] suggested that a solvent such as ether may well extract both the neutral and the singly negatively charged thiocyanate complexes. But the same study showed that solutions of trioctylphosphine oxide $(C_8H_{17})_3PO$ in carbon tetrachloride are only likely to extract the neutral complex.

In this paper we use our data on the extraction of iron by 2×10^{-4}M-$(C_8H_{17})_3PO$ in carbon tetrachloride from aqueous thiocyanate solutions of various concentrations to calculate the stability constants of the thiocyanate complexes of iron and the partition coefficient for the neutral complex. We then apply these constants to our data for other solvent dilutions and obtain partition coefficients for both the neutral and singly negatively charged species.

EXPERIMENTAL

The methods were reported in Part IV.[7] The ionic strength of the aqueous phase was maintained at 2M by sodium perchlorate and its acidity at 0·01M by perchloric acid. The iron concentration was *ca.* 10^{-6}M. The organic phases used were (i) 2×10^{-4}M-trioctylphosphine oxide $[(C_8H_{17})_3PO]$ in carbon tetrachloride, (ii) $5{\cdot}4 \times 10^{-3}$M-butyl dibutylphosphinate ($Bu_2PO{\cdot}OBu$) in carbon tetrachloride, (iii) 10^{-2}M-dibutyl butylphosphonate $[BuPO(OBu)_2]$ in carbon tetrachloride, and (iv) $1{\cdot}47 \times 10^{-1}$M-tributyl phosphate $[(BuO)_3PO]$.

Equilibration was conducted in a thermostat maintained at 20·00 ± 0·01 °C. Measurement was made of the distribution coefficient as a function of the concentration of thiocyanate in the aqueous phase. For solutions containing less than 0·01M-thiocyanate a correction was made for ferric perchlorate extraction. Between 30 and 40 measurements were made on each system.

RESULTS AND DISCUSSION

The primary data are shown in the four plots in Figure 1. If the usual assumption is made that under the conditions of these measurements the activity coefficients can be considered constant, in a system where only a single complex is extracted the distribution coefficient, D, is given by expression (1) where the β_i are the cumulative stability constants, [L] the concentration of the ligand, P the partition coefficient for the extracting complex, and c the number of ligand units in the extracting species. In experiments with dilute solutions of an active extractant in an inert diluent, P will be a function of the concentration of the extractant. Expression (1) can easily be transformed into the more convenient polynomial form (2) where $y = [L]^c/D$; $x = [L]$, and $a_i = \beta_i/P\beta_c$. If J experimental determinations have been made of x and y a least-squares calculation of the a_i, and hence the β_i, leads to the determination of the minimum of expression (2), where

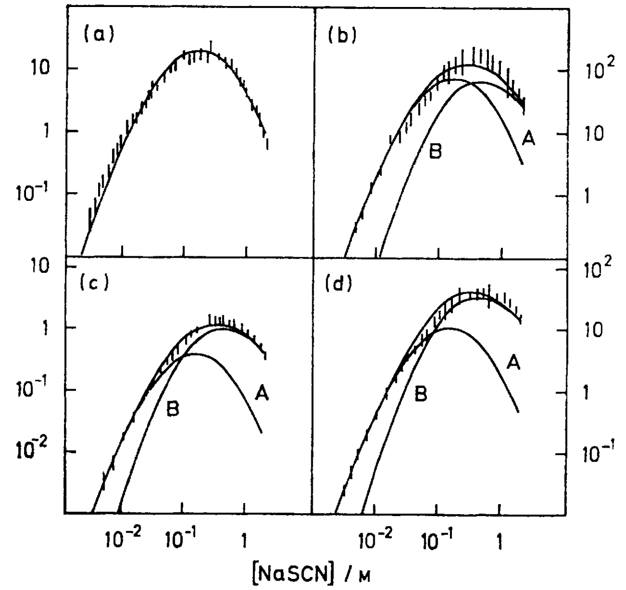

FIGURE 1 The extraction of tracer iron into organophosphorus solvents as a function of the thiocyanate concentration: A, theoretical contribution of neutral complex; B, theoretical contribution of anionic complex; (a) $(C_8H_{17})_3PO$; (b) $Bu_2PO{\cdot}OBu$; (c) $BuPO(OBu)_2$; (c) $(BuO)_3PO$

$$D = P \,.\, \beta_c[L]^c/\sum_{i=0}^{n}\beta_i[L]^i \qquad (1)$$

$$y = \sum_{i=0}^{n} a_i x^i \qquad (2)$$

$$\psi^2 = \sum_{j=1}^{J} w_j(y_j - \sum_{i=0}^{n} a_i x_j^i)^2 \qquad (3)$$

the w_j are the weights assigned to the experimental values (x_j,y_j). These weights are calculated from the relation $w_j = 1/\sigma_j^2$, where the σ_j are the standard deviations of the measurements. Differentiation of ψ^2 with respect to the adjustable parameters a_i gives a system of linear equations such as (4) and (5). These

$$a_0 \sum_j w_j + a_1 \sum_j x_j + \cdots + a_n \sum_j w_j x_j^n = \sum_j w_j y_j \qquad (4)$$

$$a_0 \sum_j w_j x_j^n + \cdots + a_n \sum_j w_j x_j^{2n} = \sum_j w_j y_j x_j^n \qquad (5)$$

are solved for the desired parameters a_i. The array of equations such as (4) and (5) can be expressed in matrix notation $W\mathbf{A} = \mathbf{Y}$ where W is the $(n + 1) \times (n + 1)$ matrix of the coefficients $\sum_j w_j x_j^n$, $\mathbf{A}$ is the column vector defined by the a_i, and $\mathbf{Y}$ is the column vector

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[7] Part IV, A. G. Maddock and (the late) L. O. Medeiros, *J. Chem. Soc.* (*A*), 1969, 1946.

of the coefficients $\sum_j w_j y_j x^n$. Thus the a_i can be determined by calculating the inverse matrix W^{-1} and multiplying both sides of equation (4), so that $\mathbf{A} = W^{-1}\mathbf{Y}$.

Computer treatment of such data is rather simple when a matrix inversion subroutine is available. However when a programme written on this basis was applied to the data, negative values for some of the stability constants were obtained.

Rydberg *et al.*[8] and others have had similar difficulties using equivalent procedures for the analysis of solvent extraction data. They considered that this was, in fact, an advantage of the least-squares technique: such results simply meant that the data were not good enough to enable all the constants to be obtained. If values could be estimated from the data in some other way, for example by use of a graphical procedure, this simply reflected the fact that other procedures often fail to yield standard errors and if these were determined they would exceed 100%.

TABLE 1

Successive stability constants

log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	t/°C	Salt concn.	$[H^+]$/M	Ref.
2·3	1·94	1·4	0·8	0·02		Room	?	?	1
2·09	1·75	−0·74	1·80	−0·70	−1·03	18	1·8M-$NaClO_4$	0·18	2
1·95	2·02	−0·41	−1·14	−1·57	−1·51	18	1·8M-KNO_3	0·18	2
2·35	1·55	1·31	0·66	0·21		*ca.* 18	1·4M-$HClO_4$	1·4	3
2·1	1·3	0·5	0	−0·1	−0·1	22	4M-$NaNO_3$	0·2	4
2·18	1·42	1·40	1·30	−0·07	−0·09	25	3M-$LiClO_4$	0·2	5
(2·09)	1·48	1·00	0·67	0·18	−0·6	20	2M-$NaClO_4$	0·2	This work

The argument that if particular parameters cannot be established by this least-squares procedure, they also cannot be evaluated by methods of successive approximation or graphical procedures seems quite secure. But the numerical process of matrix inversion can be liable to errors. If the matrix is ill-conditioned,[9] which may occur if two rows of the matrix W define planes which are almost parallel and the determinant of W becomes very small, quite large errors may enter the inversion process. Alternative treatments of the data have therefore been sought.

The logarithmic plot of the data (Figure 1,A) seemed to display the symmetry with respect to a vertical line drawn at [SCN] = *ca.* 0·21M noted by Macdonald *et al.*[2] As the latter authors have shown, such symmetry implies a relation between β_0 and β_6, β_1 and β_5, and β_2 and β_4. The solution of the data is thus reduced to the evaluation of only three parameters, if use is made of spectroscopic data for β_1. However, when these data were treated in this way a negative value for β_3 was obtained and the ψ^2 of the fit to the data was poor. Macdonald *et al.*[2] also failed to obtain any reasonable precision in their evaluation of β_3.

There remains the possibility of assuming a relationship between all the successive stability constants. Such an assumption is often made in the graphical treatment of such data.[10] Calculations have been carried out on two alternative assumptions. The first is to suppose K_i/K_{i+1} is constant, k. The second induces a statistical term and supposed $K_i/K_{i+1} = i(n-i)/(n-i+1)(i+1)k'$. However, solution for P, k (or k'), and K_1 is not a simple linear problem involving a polynomial, so we chose a best value of K_1 from the literature[2,5,11] and a method of successive approximation for P and k (or k'). The value $K_1 = 125$ was taken as appropriate to the ionic strength and temperature in this study. For each set of β_i thus calculated the P was determined by least squares, the extraction curve was drawn by the computer, and the variance of the fit with the prime data was calculated. This method is essentially Sillén's two-parameter method but with the computer to calculate and draw the curves and assess the quality of the fit. A short computation soon showed that the assumption $K_i/K_{i+1} = k$ would not give a good fit. But a value of $k' = 1·65$ gave a satisfactory fit.

Rydberg[12] has observed that the consistency of the calculated parameters, measured values, and their estimated errors, can be assessed by comparing the quality of the fit, measured by the sum of the weighted, squared residuals with the value expected for a ψ^2 distribution. For the solution mentioned above the sum of the squared residuals was very large if the weights were calculated entirely on the basis of the counting errors in the measurements. If however they were calculated from the errors estimated from the spread of repetitive but independent measurements, or from the scatter of the measurements about a smooth curve, this sum fell to *ca.* 40, that is to say about the number of degrees of freedom of the system. Equally satisfactory agreement was obtained in the further calculations made for the other system so that we believe that our calculated stability constants are significant. The full line in Figure 1,A shows the fit of the calculated curve to our data. Table 1 compares the successive stability constants K_i with previously reported values.

The other extractant solutions used are more likely to extract both $Fe(SCN)_3$ and $Fe(SCN)_4^-$. The expression appropriate for the distributive coefficient

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[8] J. Rydberg, *Acta Chem. Scand.*, 1961, **15**, 1723.

[9] T. R. McCalla, 'Introduction to Numerical Methods and FORTRAN Programming,' Wiley, New York, 1967.

[10] F. J. C. Rossotti and H. Rossotti, 'The Determination of Stability Constants,' McGraw-Hill, New York, 1961.

[11] V. E. Miranov and Yu. I. Rutkovskii, *Zhur. neorg. Khim.*, 1965, **10**, 2670; V. N. Vasil'eva and V. P. Vasil'ev, *Izvest. V.U.Z. Khim. i Khim. Teknol.*, 1966, **9**, 185; J. Maslowska, *Roczniki Chem.*, 1968, **42**, 1819.

[12] J. Rydberg and J. C. Sullivan, *Acta Chem. Scand.*, 1959, **13**, 2057.

depends on whether or not the $Fe(SCN)_4^-$ dissociates from its co-cation in the organic phase. If there is negligible dissociation we may write equation (6)

$$D = P_3\beta_3[L]^3/\sum_{i=0}^{n} P_i[L]^i + P_4\beta_4[L]^4/\sum_{i=0}^{n} \beta_i[L]^i \quad (6)$$

while if dissociation is almost complete we have[13] equation (7), assuming extraction of the complex acid

$$D = P_3\beta_3[L]^3/\sum_{i=0}^{n} \beta_i[L]^i + P_4\beta_4[L]^{3\cdot5}/\sum_{i=0}^{n} \beta_i[L]^i \quad (7)$$

and tracer concentration of the metal.

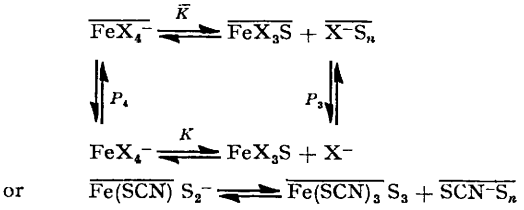
Attempts were made to fit the data for $Bu_2PO{\cdot}OBu$, $BuPO(OBu)_2$, and $(BuO)_3PO$ solutions to these equations by use of the β_i established above and a least-squares approach. Equation (6) was found to describe the data satisfactorily while (7) did not. With values of P_3 and P_4 evaluated in this way the ψ^2 of the fit was close to the number of degrees of freedom for both the $Bu_2PO{\cdot}OBu$ and $BuPO(OBu)_2$ data, the same order of errors being assumed in the measurements as in the calculation of the β_i. The $(BuO)_3PO$ data however gave nearly twice as large a ψ^2.

The partition coefficients calculated in this way are shown in Table 2. The values in the third and fourth columns are those relating to the dilutions used. The values in the fifth and sixth columns are calculated values for the pure solvents from the dilution data established in a previous paper.[7]

The results suggest that extraction of both species is important over a considerable range of thiocyanate concentrations.

The symmetrical shape of the plots of log D against $[SCN]^-$ and the underlying relation between the k_i reflect the result, reported in a previous paper, that all the thiocyanate complexes are six-co-ordinate. In the bromo- and, especially, the chloro-systems where there is reason to suppose that a change in co-ordination number from 6 to 4 takes place, no simple relation between all k_i can be expected and indeed the experimental data yield markedly asymmetric curves. Some results were given in Figure 4 in Part IV for the chloride and bromide systems.

It may be observed that the dilution data (*cf.* Part IV [7]) gave no evidence for the presence of two thiocyanate species with any of the extractants, but reasons for distrusting a naïve analysis of dilution data have been given [7] and the present evidence is regarded as much more trustworthy. If two complexes can extract (Scheme 1), only three of K, $\bar{K}$, P_3, and P_4 can be independent.



SCHEME 1

(The bars denote species in the organic phase.) By considering P_3 or P_4 as the dependent variable one can see that whether the extraction of the anionic or neutral species dominates the system will depend on the co-ordination competition of the ligand and the solvent as well as the independent partition coefficient. Thus one can expect that with poorly donating but high dielectric constant solvents extraction of the anionic complex will be favoured. But that strong donor solvents like $(C_8H_{17})_3PO$ will favour the extraction of neutral species.

TABLE 2

Partition coefficients for ferric thiocyanate complexes

Solvent	Mole fraction extractant	P_3 $Fe(SCN)_3$	P_4 $Fe(SCN)_4^-$	Extrapolated to pure solvent $Fe(SCN)_3$	$Fe(SCN)_4^-$
$(C_8H_{17})_3PO$	$2{\cdot}20 \times 10^{-5}$	53·3		5×10^{15}	
$Bu_2PO{\cdot}OBu$	$5{\cdot}30 \times 10^{-5}$	186	154	$1{\cdot}24 \times 10^{12}$	$1{\cdot}02 \times 10^{12}$
$BuPO(OBu)_2$	$1{\cdot}00 \times 10^{-3}$	1·02	2·33	$1{\cdot}03 \times 10^{9}$	$2{\cdot}33 \times 10^{9}$
$(BuO)_3PO$	$1{\cdot}47 \times 10^{-2}$	27·4	80·1	$8{\cdot}61 \times 10^{6}$	$25{\cdot}1 \times 10^{6}$

The Temperature-coefficient of the Extraction.—Although there are many data on the effect of temperature on the solvent extraction of different inorganic species, a detailed analysis of the factors involved has seldom been made.

Let us examine the case of a single extracting complex, ML_c. Equilibria (8)—(10) are involved, besides

$$\bar{S} \rightleftharpoons S \quad (8)$$

$$ML_c + nS \rightleftharpoons ML_cS_n \quad (9)$$

$$\overline{ML_cS_n} \rightleftharpoons ML_cS_n \quad (10)$$

the complexing of the metal, M, by the ligand, L, where the complex ML_c extracts as the solvate ML_cS_n and the bars indicate the organic phase. These equilibria are determined by the constants k_S, k_c, and k_E, respectively. If very little of the solvated extracting complex remains in the aqueous phase, as found above, then for ideal behaviour we obtain equation (11) where

$$D = \frac{[\overline{ML_cS_n}]}{\sum_i [ML_i]} = \frac{k_c k_E}{k_S^n} \cdot \frac{[\bar{S}]^n \beta_c [L]^c}{\sum_i \beta_i [L]^i} \quad (11)$$

the square brackets denote concentrations. For real systems this becomes (12) where g_L is the activity coefficient of the ligand in the aqueous phase, g_i is the activity coefficient of the ith complex in the aqueous phase, $\bar{f}$ is the activity coefficient of the solvating

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[13] A. G. Maddock, W. Smulek, and A. J. Tench, *Trans. Faraday Soc.*, 1962, **58**, 923.

solvent in the organic phase, and $\bar{h}$ is the activity coefficient of the solvated extracting complex in the

$$D = \frac{k_c k_E}{k_s^n} \cdot \frac{\bar{f}^n}{\bar{h}} \cdot \frac{\beta_c[L]^c}{\sum\limits_i \beta_i[L]^i} \cdot \frac{g_L{}^c}{(g_L{}^i/g_i)} \qquad (12)$$

organic phase. Differentiating (12) in logarithmic form one obtains equation (13) where c.c. means constant

$$\left[\frac{\partial \log D}{\partial T}\right]_{\text{c.c.}} = \frac{\partial \log(k_c \cdot k_E/k_s{}^n)}{\partial T} + \frac{\partial \log \beta_c}{\partial T} + \frac{\partial \log(\bar{f}^n/\bar{h})}{\partial T} + \frac{\partial \log g_L{}^c}{\partial T} - \frac{\log \sum\limits_i \beta_i[L]^i(g_L{}^i/g_i)}{T} \qquad (13)$$

composition of the system. Now the first term is $\Delta H_E/RT^2$ and the second $\Delta H_c°/RT^L$, where ΔH_E is the standard enthalpy of extraction of the complex and $\Delta H_c°$ its standard enthalpy of formation. Further, we have equations (14) and (15) where α_i is the fraction

$$\frac{\partial \log \sum\limits_i \beta_i[L]^i(g_L{}^i/g_i)}{\partial T} = \frac{\sum\limits_i \beta_i[L]^i(g_L{}^i/g_i)\dfrac{\partial \log \beta_i}{T}}{\sum\limits_i \beta_i[L]^i(g_L{}^i/g_i)} + \frac{\sum\limits_i \beta_i[L]^i(g_L{}^i/g_i)\dfrac{\partial \log(g_L{}^i/g_i)}{\partial T}}{\sum\limits_i \beta_i[L]^i(g_L{}^i/g_i)} \qquad (14)$$

$$= \frac{\sum\limits_i \alpha_i \Delta H_i°}{RT^2} + \sum_i \alpha_i \frac{\partial \log(g_L{}^i/g_i)}{\partial T} \qquad (15)$$

of the complex ML_i. Thus we have equation (16).

$$\frac{\partial \log D}{\partial T} = \frac{\Delta H_c°}{RT^2} + \frac{\Delta H_E°}{RT^2} - \sum_i \alpha_i \frac{\Delta H_i°}{RT^2} + \frac{\partial \log g_L{}^c}{\partial T} - \sum_i \alpha_i \frac{\partial \log(g_L{}^i/g_i)}{\partial T} + \frac{\partial \log(\bar{f}^n/\bar{h})}{\partial T} \qquad (16)$$

For the standard state it is convenient to choose for the ligand, metal ion, and the complexes the hypothetical aqueous solution where the analytical concentrations of the metal and ligand are unity but the ionic strength is equal to that of the aqueous phase used in the experiments. This aqueous phase is taken to be in equilibrium with the standard state of the organic phase. Thus g_L, g_i, and $h \longrightarrow 1$ as [L] and [M] $\longrightarrow 0$. Thus for tracer concentration of the extracting metal (16) may be approximated by (17). where $RT^2\overline{\Delta H}_s = (\partial \log \bar{f})/\partial T$ and $\overline{\Delta H}_s$ is the partial entropy of mixing

$$\frac{\partial \log D}{\partial T} = \frac{\Delta H_E°}{RT^2} + \frac{\Delta H_c°}{RT^2} - \sum_i \alpha_i \frac{\Delta H_i°}{RT^2} + \frac{n\overline{\Delta H}_s}{RT^2} \qquad (17)$$

of the solvents in the organic phase (solvating solvent and diluent). This term can be eliminated by choosing as standard state the particular solvent–diluent mixture used in the experiments, but for comparing solvents at different dilutions it is perhaps better to choose a particular molarity as the standard. For athermal mixtures the term vanishes and for the moment this will be assumed to be the case.

A more useful equation for deciding what approximations are valid can be obtained as follows. At constant temperature, we obtain equation (18) when $\bar{n}$, given

$$\frac{\partial \log \alpha_i}{\partial \log [L]} = i - \bar{n} \qquad (18)$$

$$\bar{n} = \frac{\sum\limits_i \beta_i[L]^i}{\beta_i[L]^i} \qquad (19)$$

by (19), is Bjerrum's degree of formation of the system. But we also have equation (20) and thus (21). Integrating between two ligand concentrations L_0 and L_1 we obtain equation (22) [or (23)] whence equation (24)

$$\frac{\partial \log D}{\partial \log [L]} = c - \bar{n} \qquad (20)$$

$$\frac{\partial \log \alpha^i}{\partial \log [L]} - \frac{\log D}{\log [L]} = i - c \qquad (21)$$

$$\int_{(\alpha_i)_0}^{(\alpha_i)_1} \mathrm{d} \log \alpha_i - \int_{D_0}^{D_1} \mathrm{d} \log D = (i - c) \int_{L_0}^{L_1} \mathrm{d} \log [L] \qquad (22)$$

or
$$(\alpha_i)_1 = (\alpha_i)_0 \frac{D_1}{D_0}\left(\frac{L_1}{L_0}\right)^{i-c} \qquad (23)$$

$$\left(\frac{\partial \log D}{\partial T}\right)_{L_i} = \frac{\Delta H_E°}{RT^2} + \frac{\Delta H_c°}{RT^2} - \frac{D_1}{D_0}(\alpha_i)_0 \cdot \left(\frac{L_1}{L_0}\right)^{i-c} \frac{\Delta H_i°}{RT^2} \qquad (24)$$

follows. Equation (24) shows that when $D_1/D_0 \leqslant 1$ with $L_1 \leqslant L_0/10$ the terms in $(\alpha_i)_0\Delta H_i°$ for $i > c$ can be ignored and, in principle, the temperature dependence of D involves only $c + 1$ unknowns. One can conclude that plots of log D against T (or $1/T$) will, in general, be curved. Explicit equations for such curves cannot be obtained and we shall treat our data by fitting it to a polynomial by a least-squares method, increasing the order until the fit first becomes acceptable (ψ^2 test) and then differentiating the equation obtained.

(a) *Ferric Thiocyanate.*—The effect of temperature on the distribution coefficient of ferric thiocyanate was explored by use of solvents in which extraction of the uncharged complex is dominant.[7] Measurements were carried out by the techniques already described, at an acidity of 0·01M and ionic strength of 2M. Results for 2×10^{-4}M-$(C_8H_{17})_3PO$ in CCl_4 are shown in Figure 2 for several concentrations of thiocyanate in the aqueous layer. The data could be fitted satisfactorily to quadratic expressions in $T \log D = a + bT + cT^2$. The results are given in Table 3, together with data for the other solvents, although for the other three solvents measurements were only made at one concentration of thiocyanate.

Figure 2 shows that the extraction of ferric thiocyanate is very exothermic; the distribution coefficient almost doubles if the temperature is lowered by only

5 K. Careful thermostatic control is essential for the study of this system.

The data in Table 3 give a difference in slope at 20 °C in 0·01 and 0·1M-thiocyanate which is not much different from the uncertainty in the data. The composition of the aqueous phase, as was seen above changes considerably between these concentrations; the percentage of $Fe(SCN)_3$ rises from 1·52% in 0·01M-NaSCN to 35·1% in 0·1M-NaSCN. This shows that the enthalpies of formation of the complexes make only a small contribution to the temperature coefficient in this system, too small for any estimate of their value. Published values of ΔH_1° are $-1\cdot 6$ and $-1\cdot 9$ kcal mol^{-1} respectively.[14] The dependence of $(\partial \log D)/\partial T$ on the concentration of sodium thiocyanate arises only from the term $-\sum_i \alpha_i \Delta H_i^\circ$ in equation (17) and the above values suggest only a weak dependence, as observed.

TABLE 3

Temperature dependence of the extraction of ferric thiocyanate

($\ln D = a + bT + cT^2$)

Solvent	[NaSCN]/M	a	b	c	$RT^2\, d\ln D/dT$ kcal mol^{-1} at 20 °C
$(C_8H_{17})_3PO$	0·01	1·82 ± 0·16	−0·13 ± 0·02	(1·5 ± 2·5) × 10^{-4}	−22·4 ± 3
	0·015	2·46 ± 0·06	−0·123 ± 0·007	(0·5 ± 1·7) × 10^{-5}	−21·2 ± 1
	0·025	3·25 ± 0·21	−0·134 ± 0·004	(5·1 ± 1·9) × 10^{-4}	−19·6 ± 2
	0·04	4·02 ± 0·05	−0·147 ± 0·004	(7·3 ± 0·9) × 10^{-4}	−20·1 ± 1
	0·06	4·27 ± 0·5	−0·15 ± 0·01	(1·1 ± 0·5) × 10^{-3}	−18·9 ± 2
	0·10	4·29 ± 0·1	−0·10 ± 0·002	(0·3 ± 2) × 10^{-4}	−17·2 ± 2
$Bu_2PO{\cdot}OBu$	0·01	0·23 ± 0·05	−0·155 ± 0·006	(7 ± 1·5) × 10^{-4}	−21·8 ± 2
$BuPO(OBu)_2$	0·01	−2·28 ± 0·02	−0·131 ± 0·003	(7·6 ± 1) × 10^{-4}	−17·4 ± 0·7
$(BuO)_3PO$	0·01	0·77 ± 0·05	−(9·78 ± 0·7) × 10^{-2}	(0·7 ± 2) × 10^{-4}	−16·3 ± 2

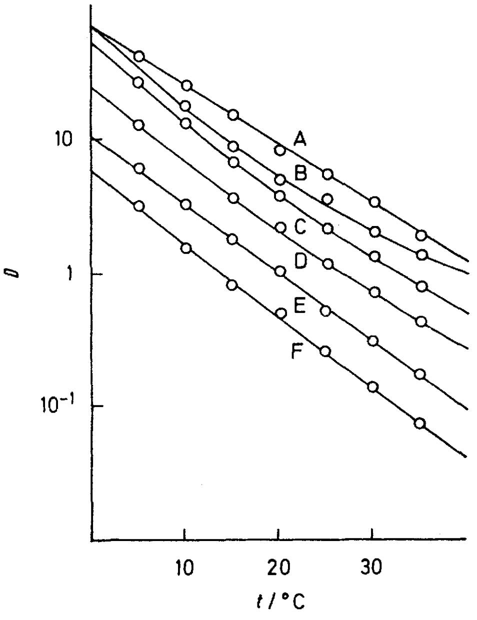

FIGURE 2 The influence of the temperature on the extraction of ferric thiocyanate into trioctylphosphine oxide from solutions of different concentrations of sodium thiocyanate. The curves are quadratics, fitted by the method of least-squares; molarity of NaSCN: A, 0·1M; B, 0·06M; C, 0·04M; D, 0·025M; E, 0·015M; F, 0·01M

In 0·1M-NaSCN the data from the Introduction show the proportion of the six $Fe(SCN)_n$ ($n = 1$—6) complexes to be 10·8, 34·3, 35·1, 16·4, 2·4, and 0·09%. Supposing all the ΔH_i° are of the order of $-1\cdot 5$ kcal mol^{-1}, then $\Delta H_c^\circ - \alpha_i \Delta H_i^\circ = ca.$ 0 cal mol^{-1} or, if we take $\Delta H_i^\circ \approx i\Delta H_1^\circ = 1\cdot 5i$ kcal mol^{-1}, then $\Delta H_c^\circ - \sum \alpha_i \Delta H_i^\circ = ca. -800$ cal mol^{-1}. The experimental error, however, corresponds to about ±2 kcal mol^{-1}. Thus ΔH_E° can be taken as -17 ± 2 kcal mol^{-1}. The temperature-dependence studies on the four organophosphorus solvents were carried out only from 0·01M-NaSCN. At this concentration the percentage of iron present in the anionic forms in the aqueous layer is very small (see Introduction). The concentrations of $Bu_2PO{\cdot}OBu$, $BuPO(OBu_2)$, and $(BuO)_3PO$ were $5\cdot 4 \times 10^{-3}$, 0·01, and 0·14M respectively in CCl_4. The corrections necessary for the contribution from the complexing equilibria in the aqueous phase can be estimated from the $(C_8H_{17})_3PO$ data. These give equation (25). The data are in Figure 3. Combining

$$\left(\frac{\partial \log D}{\partial T}\right)_{\cdot 01\mathrm{M}} - \left(\frac{\partial \log D}{\partial T}\right)_{0\cdot 1\mathrm{M}} = 5\cdot 2 \text{ kcal mol}^{-1} \quad (25)$$

these data with the equilibrium data (Introduction) one obtains for the thermodynamic functions for the extraction processes the values given in Table 4. It is interesting to compare these data with those reported for the same solvents for uranyl nitrate.[15] The lowest enthalpy change for ferric thiocyanate, 11·1 kcal mol^{-1}, is significantly higher than for the uranium salt. The trends in the entropy changes are similar for the two metals. It will be noted that the favourable positive entropy change in the case of trioctylphosphine oxide

TABLE 4

Thermodynamics of the extraction of ferric thiocyanate

Solvent	ΔG° kcal mol^{-1}	ΔH° kcal mol^{-1}	ΔS° cal mol^{-1} K^{-1}
$(C_8H_{17})_3PO$	−21·2	−17·2	14
$Bu_2PO{\cdot}OBu$	−16·3	−16·6	1
$BuPO(OBu)_2$	−12·2	−12·2	0
$(BuO)_3PO$	−9·3	−11·1	−6

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[14] V. P. Vasil'ev and P. S. Mukhina, *Izvest V.U.Z: Khim. i. Khim. Teknol.*, 1969, **12**, 258; G. S. Laurense, *Trans. Faraday Soc.*, 1956, **52**, 236; R. H. Betts and F. S. Dainton, *J. Amer. Chem. Soc.*, 1953, **75**, 5721.

[15] T. H. Siddall, *J. Amer. Chem. Soc.*, 1954, **81**, 4176.

makes an appreciable contribution to the free energy of extraction.

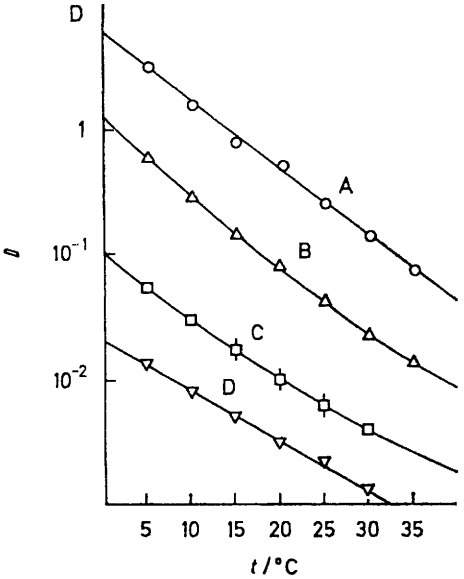

FIGURE 3 The influence of the temperature on the extraction of ferric thiocyanate from 0·01M-NaSCN solutions into A, $(C_8H_{17})_3PO$; B, $Bu_2PO{\cdot}OBu$; C, $BuPO(OBu)_2$; and D, $(BuO)_3PO$. The curves are quadratics, fitted by the method of least squares. For curves B and C, values of D have been multiplied by 0·1 and for curve D by 0·001

(*b*) *Ferric Halides*.—For comparison some measurements have also been made on ferric chloride and bromide extraction. For ferric bromide an 0·01M solution of trioctylphosphine oxide in CCl_4 was used as extractant. The aqueous phase was 0·05M in acid. The results obtained at different concentrations of sodium bromide are shown in Figure 4.

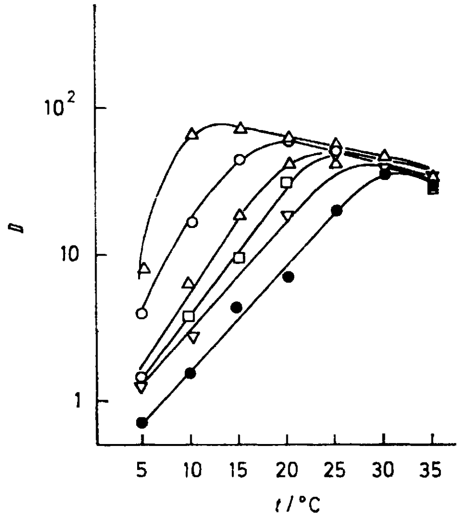

FIGURE 4 The influence of the temperature on the extraction of ferric bromide into 0·01M-trioctylphosphine oxide in CCl_4 from solutions of the following NaBr concentrations: △, 0·6M; ○, 0·4M; △, 0·3M; □, 0·25M; ▽, 0·2M; ●, 0·15M

For each solution the extraction shows a maximum at a temperature which is dependent on the sodium bromide concentration. This behaviour is exactly what can be expected if $\Delta H_E°$ and $\Delta H_i°$ have different signs, with $\Delta H_E°$ negative. In fact, the published enthalpy of formation of the first bromo-complex of the ferric ion, 6·1 kcal mol^{-1} is indeed positive.[16]

Figure 4 also shows that at high enough temperatures all the distribution coefficients lie on the same curve, independent of the concentration of bromide. This is only possible if at high enough temperature the aqueous phase contains predominantly the extractable complex. This implies that for the concentrations of bromide explored comparatively little formation of anionic complexes occurs. The decrease in extraction in the high-temperature region is thus determined by the enthalpy of extraction. Graphical differentiation gives $\Delta H_E° = -7$ kcal mol^{-1}, but the probable error is large, ±30%. Data for the extraction of ferric chloride are in Figure 5. The general features are similar to the bromide data and imply that $\Delta H_E°$ and $\Delta H_i°$ are of opposite sign. The published enthalpy of formation of the first chloro-complex is 8·5 kcal mol^{-1},[16] in agreement with this interpretation. The chloride data do not, however, tend to chloride concentration-independent values at high temperatures, at least in the range of temperatures studied, suggesting that formation of anionic complexes is much more important in this system. If one supposes that at the highest concentration of chloride used, 0·12M, the descending portion of the curve is entirely due to the enthalpy of extraction, one obtains a $\Delta H_E°$ of $-10{\cdot}5$ kcal mol^{-1}. The data of Gamlen and Jordan[17] indeed support the hypothesis that the neutral chloro-complex will predominate in such situations. At least the results sug-

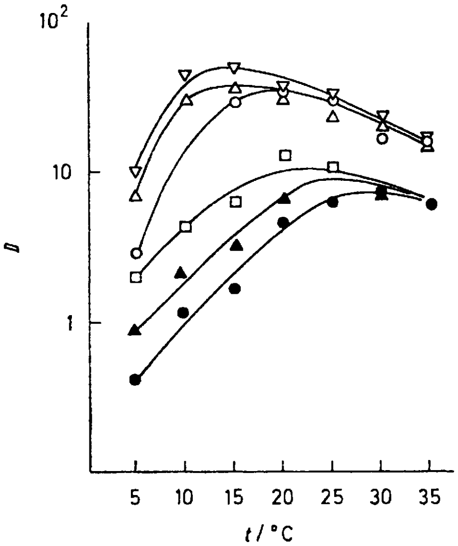

FIGURE 5 The influence of the temperature on the extraction of ferric chloride into 0·01M-trioctylphosphine oxide in CCl_4 from solutions of the following NaCl concentrations: ▽, 0·12M; △, 0·085M; ○, 0·065M; □, 0·045M; ▲, 0·03M; ●, 0·02M

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[16] E. Rabinowitch and W. H. Stockmeyer, *J. Amer. Chem. Soc.*, 1942, **64**, 335.

[17] G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1953, 1435.

gest that the enthalpies of extraction of the chloro- and bromo-complexes are not greatly different, with the latter being a little less negative. Combining these data with the free energies of extraction of —2 and —2·5 kcal mol^{-1} for the chloro- and bromo-complexes one obtains entropies of extraction of —29 and —15 cal mol^{-1} K^{-1}. Thus the less favourable enthalpy of extraction of the bromo-complex is compensated by a more favourable entropy term so that both halides show comparable extractions.

Finally one can compare the extraction of the thiocyanates with the halides. In poorly donating solvents, such as nitrobenzene, their behaviour is not greatly different. Figure 2 in Part IV [7] shows that the bromide and thiocyanate systems give very similar extraction from weakly acid aqueous phases. With the strongly donating trioctylphosphine oxide, however, the thiocyanate shows a distribution coefficient of 10^6 under conditions where the bromide system gives 70.

The changes in thermodynamic functions associated with the extraction process have not been very precisely established but some conclusions seem secure. Table 5 gives values for the chloride, bromide, and thiocyanate systems calculated for 0·01M-$(C_8H_{17})_3PO$ in CCl_4. The favourable extraction of the thiocyanate must be attributed to the favourable enthalpy term. Since the Mössbauer data suggest similar co-ordination for the thiocyanate and bromide complexes and since it seems unreasonable that the enthalpies of transferring the complexes from one phase to the other should be much different, one must conclude that the solvent–metal bonds are stronger in the thiocyanate than in the bromo-complexes.

TABLE 5

Approximate values of the thermodynamic functions of extraction of ferric chloride, bromide, and thiocyanate into 0·01M-trioctylphosphine oxide

	$\Delta G°$ kcal mol^{-1}	$\Delta H°$ kcal mol^{-1}	$\Delta S°$ cal mol^{-1} K^{-1}
Chloride	−2	−10	−28
Bromide	−2·5	−7	−15
Thiocyanate	−9·1	−17·2	−27

We thank the Laboratorio di Fisica e Engenharia Nucleares, Sacavem, Portugal for leave and support (to L. O. M.).

[2/2493 *Received, 6th November, 1972*]