

Studies on Cobaltamines

III. Some Evidence on the Association of Thiocyanate and Perchlorate Ions with the *trans*-Dithiocyanatobis(ethylenediamine) Cobalt(III) Ion

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The extraction of *trans*-[Co en₂(SCN)₂]SCN from aqueous solutions of varying NH₄SCN concentration into a SCN⁻-saturated anion-exchange resin and also into a mixture of *cyclohexanone* and 2-octanol has been recorded. In both cases a maximum of the extraction quotient was found at about $C_{\text{NH}_4\text{SCN}} = 1$ M. This is interpreted as an indication of outer-sphere complex formation.

By a conventional solubility method the first association constant for the reaction between the SCN⁻ and *trans*-Co en₂(SCN)₂⁺ ions has been determined at an ionic strength of 3 M (NaClO₄). $\beta_1 = 0.3_0$ M⁻¹. This result is discussed in relation to a hypothesis of competing association of SCN⁻ and ClO₄⁻ ions with the complex ion.

Some extraction experiments from solutions of varying concentrations of NaClO₄ into two different ketonic solvents are also recorded. These results are not conclusive in regard to the question of perchlorate outer-sphere complexes.

Several reports on the formation of "outer-sphere complexes" have recently been compiled^{1,2}. However, some authors seem to regard this kind of association as an "ion-pairing" in the sense of Bjerrum³. This point of view is rather trivial in that effects thus described could equally well be accounted for by a calculation of the coefficients of activity of the reacting ions from the equation deduced by Gronwall, LaMer and Sandved⁴ or by any still more elaborated treatment.

Therefore it was considered important to demonstrate the existence or non-existence of association in water between some univalent and rather large ions, where "ion-pairs" are not likely to be formed, *i.e.*, where the high order terms in the equation of Gronwall *et al.*⁴ can be ignored. Such ions are even less expected to form "triple ions" in the sense of Fuoss and Kraus⁵.

As such a system *trans*-Co en₂(SCN)₂⁺ and SCN⁻ has been chosen.

The investigation has been pursued along two different lines. The first one has been to decide whether anionic complexes are formed or not. The second one has been an attempt to determine at least the first association constant at a constant ionic strength.

DETECTION OF ANIONIC THIOCYANATO COMPLEXES

Methods and Notations

It has been shown by Fronæus^{6,7} that anionic complexes can be detected with the help of anionic exchange resins. If the distribution of metal between the resin, saturated with the ligand, and the aqueous phase is determined as a function of the ligand concentration in the aqueous phase, then a maximum of that function will indicate the formation of at least one anionic complex.

The detailed deductions are found in the papers referred to. We employ the following symbols:

M	=	<i>trans</i> -Co en ₂ (SCN) ₂ ⁺
B	=	SCN-
C _M	=	total concn. of M in the aqueous phase
C _{MR}	=	» » » M » » resin »
C _B	=	» » » B » » aqueous »

What we intend to measure is thus $\varphi_R = \frac{C_{MR}}{C_M}$ as a function of C_B .

Likewise, if the distribution of metal between an organic solvent and the aqueous phase is determined at various C_B , then a maximum might be obtained. If it is assumed that only the neutral complex is extracted, this maximum may be taken as an indication of the existence of anionic complexes in the aqueous phase. Activity changes in the organic phase may, however, make the interpretation uncertain. It was found that a mixture of equal volumes of *cyclohexanone* and 2-octanol was a good extracting solvent for *trans*-Co en₂(SCN)₂ SCN. If C_{MS} is the concentration of M extracted into this solvent mixture we will measure $\varphi_S = \frac{C_{MS}}{C_M}$ as a function of C_B .

Measurements

Chemicals used. *Trans*-Co en₂(SCN)₂ClO₄ was prepared from analytical grade chemicals following Werner and Bräunlich⁸, with the modification that the perchlorate was precipitated by concentrated perchloric acid from the mixture of *cis*- and *trans*-isomers. It was found rather unexpectedly that the *cis*-isomer was precipitated with very great difficulty, so that an apparently pure *trans*-Co en₂(SCN)₂ClO₄ was obtained after two reprecipitations. The crystal mass was washed acid-free with ethanol and ether and air-dried. The absorption spectrum of the product compares rather well with the data of Shimura^{9,10}. ($\lambda_{\max_1} = 510 \text{ m}\mu$, $\epsilon_{\max_1} = 2.82 \times 10^3$; $\lambda_{\max_2} = 315.5 \text{ m}\mu$, $\epsilon_{\max_2} = 3.08 \times 10^3$). The equivalent weight was determined alkalimetrically *via* an acid-saturated cation exchange resin; calc. 395; found 392. Cobalt content¹¹: calc. 14.93 %; found 14.89 %.

Ammonium thiocyanate solutions were prepared as before¹².

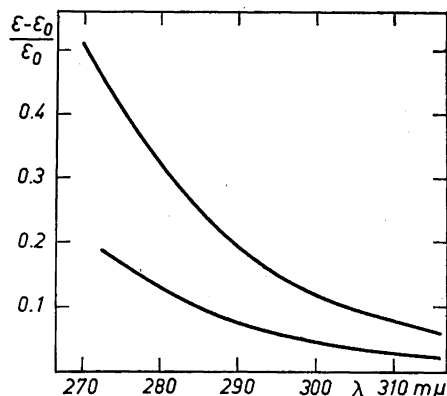


Fig. 1. The relative change of the extinction coefficients in UV. Upper curve: 0.1 mM MClO_4 + 1.5 M NaSCN (ϵ) compared to 0.1 mM MClO_4 + 1.5 M NaClO_4 (ϵ_0). Lower curve: 0.15 mM MClO_4 + 0.5 M NH_4SCN + 0.5 M NH_4ClO_4 (ϵ) compared to 0.15 mM MClO_4 + 1.0 M NH_4ClO_4 (ϵ_0).

The anionic exchange resin was Dowex 1, with 4% cross-linking. It was converted into the thiocyanate form by percolating a concentrated solution of potassium thiocyanate, corresponding to ten times the exchange capacity, through a column of the resin, which was afterwards well rinsed with distilled water and air-dried.

The extracting solvent. Cyclohexanone only cannot be used as an extracting solvent because of its tendency to dissolve large quantities of water and ammonium thiocyanate whereby the two-phase character of the system vanishes at rather low thiocyanate concentrations. Therefore an equal volume of 2-octanol was added to the cyclohexanone.

Cyclohexanone (Riedel-de Haën A.-G., *rein*) was purified by distillation at 153.5–7°C and 2-octanol (Eastman P 66) was distilled at 176–178°C.

Procedure. Ten milliliters of a solution of the composition C_B M NH_4SCN and C'_M M $\text{Co en}_2(\text{SCN})_2\text{ClO}_4$ were shaken in glass-stoppered bottles together with w g of the resin (where w was kept about 1.5 g) or 10 ml of the extracting solvent. The shaking was performed in a water-thermostat at 20.0°C. The shaking was carried out for two days in the ion-exchange experiments and for about 15 h in the extraction experiments. In order to prevent any photochemical decomposition of the complex the bottles were coated with black paint on the outside. (The photolysis was found to be strongly dependent on the thiocyanate concentration; cf. Adamson and Sporer¹³.) When equilibrium was reached, which was ascertained by prolonged shaking, the phases were rapidly separated — after centrifugation in the extraction case.

In the ion-exchange experiments the aqueous phase was sucked off as completely as possible with a filter-stick of large porosity. Thereafter the resin was rinsed rapidly in the shaking bottle with two 15 ml portions of distilled water, whereafter 20 ml of water were added and the bottles were subjected to renewed shaking. Then, as the thiocyanate concentration in the aqueous phase must be very low, the cobalt complex sorbed by the resin was almost quantitatively re-extracted. — This procedure was justified by preliminary experiments, that showed the elution process to be a slow one.

Determination of C_M . A photometric determination of C_M was deemed expedient in view of the intense colour of the complex. It was then necessary to investigate the influence of the thiocyanate concentration on the light absorption spectrum of the complex.

It was to be expected¹⁴, that — regardless of the degree of outersphere complex formation — this influence would be small, especially in the region of long wave lengths. This was also found to be the case. There was no variation at constant ionic strength at the 510 m μ maximum within the limits of the experimental error. (The variation recorded in column 3 of Table 3 must be an "ionic strength effect".) Fig. 1 gives the relative change of the extinction coefficient in the ultraviolet wave length region.

The measurements of the absorption spectra and the C_M determinations in the ion-exchange experiments were made with a Beckman Model DK-1 Recording Spectrophotometer.

In the extraction experiments C_M was determined (at 510 $m\mu$) with a Hilger Uvispek H 700 Spectrophotometer. In these experiments the aqueous phase only was examined; C_{MS} was determined by difference. In order to free the solutions from an eventual opalescence caused by small drops of the organic solvents separating at a possible temperature fall, one fifth of the solutions' volume of ethanol was added immediately after phase separation. This ethanol addition was found to cause an increase in the extinction coefficient of 3.7 %.

Determination of φ_R .

E' = optical density at the position of the 510 $m\mu$ maximum of a solution of composition C'_M M Co en₃(SCN)₂ClO₄ and C_B M NH₄SCN.

E_1 = optical density (at the 510 $m\mu$ maximum) of the same solution when 10 ml of it had been shaken with w g of the resin.

E_2 = optical density at the position of 316 $m\mu$ maximum of the solution obtained from the re-extraction from the resin ($d = 1$ cm).

We can now calculate φ_R in two different ways:

$$1. \quad C_{MR} = \text{const.} \frac{E' - E_1}{w} \times 10^{-2} \text{ mole/g} \quad (1)$$

$$C_M = \text{const.} E_1 \text{ mole/l} \quad (2)$$

$$\therefore \varphi_{R1} = \left(\frac{E'}{E_1} - 1 \right) \times \frac{10^{-2}}{w} \text{ l g}^{-1} \quad (3)$$

$$2. \quad C_{MR} = \frac{10^{-2} \times 2 E_2}{3.08 \times 10^3 \times w} \text{ mole/g} \quad (4)$$

$$C_M = C'_M - \frac{2 E_2}{3.08 \times 10^3} \text{ mole/l} \quad (5)$$

$$\varphi_{R2} = \frac{10^{-5} \times 2 E_2}{3.08 w \left(C'_M - \frac{10^{-3} \times 2 E_2}{3.08} \right)} \text{ l/g} \quad (6)$$

The factor 2 in eqn (4) originates from the fact that the volume of the solution which was used to extract the complex from the resin was 20 ml compared to the original solution of 10 ml. 3.08×10^3 is, as previously stated, the extinction coefficient of the complex at the second absorption maximum.

Determination of φ_S .

E_3 = optical density of the aqueous phase with an additional one fifth of ethanol measured at 510 $m\mu$.

We easily obtain

$$C_M = \frac{6}{5} \cdot \frac{E_3}{d \times 1.037 \times \epsilon} \quad (7)$$

where ϵ is the extinction coefficient at 510 $m\mu$ (2.82×10^3) and d is the thickness of the cell (2 cm).

C_{MS} is, however, not so easily obtained as there is still, in spite of the addition of 2-octanol to the cyclohexanone, a tendency for the organic solvent to extract water and NH₄SCN, whereby the volume of the organic phase (V_S) increases and the volume of the aqueous phase (V) decreases. For $C_B > 1$ M it was necessary to make a correction for this effect. Defining $q = V_S/V$ and assuming that the total volume of the two phases is constant, which was apparently true, it is easily deduced

$$C_{MS} = \frac{0.5 C'_M(1 + q) - C_M}{q} \quad (8)$$

Hence with a knowledge of q , we obtain $\varphi_S = \frac{C_{MS}}{C_M}$.

Determination of q . The quantity q was determined simply by shaking equal volumes of the organic solvent mixture and NH₄SCN-solutions in a stoppered, graduated centri-

Table 1. The variation of the volume quotient q with C'_B .

C'_B M	V	V_s	q	$\log(q-1)$	$\log C'_B$
2.730	4.20	5.7 ₉	1.38	-0.42 ₀	0.436
3.00	3.9 ₁	6.0 ₉	1.56	-0.25 ₂	0.477
3.60	2.7 ₆	7.2 ₄	2.62	0.20 ₀	0.556

fuge tube and reading the volumes. If C'_B means the thiocyanate concentration before equilibration, it was found (Table 1) that q could be related to C'_B by the relation

$$\log(q-1) = -2.7_4 + 5.2_5 \log C'_B \quad (9)$$

Results

The measurements are recorded in Tables 3 and 4. The values of φ_R as well as those of φ_S were reproducible within 1–2 %.

The value of C_B , the ligand concentration after equilibration, was determined as a function of C'_B , the original ligand concentration, by Volhard titration of the aqueous phase.

In the ion-exchange experiments the difference was found to be negligible; for the extraction system $C'_B - C_B$ is given in Table 2.

Table 2. The variation of C_B with C'_B .

C'_B M	C_B M	$\frac{C'_B - C_B}{V C'_B}$
0.2000	0.1916	0.0188
1.000	0.882	0.118
1.800	1.516	0.212
3.000	2.376	0.360

The values obtained in Table 2 were rationalized to the relation

$$C_B = C'_B - 0.119 (C'_B)^{3/2} \quad (10)$$

which was used for calculation of C_B in Table 4.

From Fig. 2 it follows that the two curves describing φ_{R_1} and φ_{R_2} do not coincide, but that the former one lies always above the latter. This might be explained by assuming that part of the complex sorbed by the resin is adsorbed

Table 3. The ion-exchange measurements.

$C'_M = 2.520$ mM						
C_B M	w g	E' 510 m μ	E_1 510 m μ	$\varphi_{R1} \times 10^3$ l/g (eqn 3)	E_2 316 m μ	$\varphi_{R2} \times 10^3$ l/g (eqn 6)
0.400	1.49 ₈	0.726	0.530	2.47	0.847	1.87
1.200	1.44 ₅	0.732	0.533	2.58	0.778	1.74
1.500	1.51 ₀	0.735	0.533	2.51	0.773	1.65
2.400	1.44 ₅	0.739	0.579	1.91	0.640	1.37
4.80	1.58 ₁	0.748	0.657	0.88	0.423	0.77

$C'_M = 2.111$ mM						
C_B	w	E'	E_1	$\varphi_{R1} \times 10^3$	E_2	$\varphi_{R2} \times 10^3$
0.200	1.49 ₇	0.603	0.465	1.98	0.596	1.50
0.400	1.42 ₁	0.603	0.440	2.61	0.681	1.86
0.800	1.46 ₅	0.608	0.434	2.74	0.696	1.86
1.200	1.40 ₈	0.607	0.442	2.65	0.668	1.83
1.500	1.52 ₃	0.611	0.440	2.55	0.656	1.67
2.400	1.46 ₇	0.613	0.478	1.93	0.534	1.34
4.80	1.45 ₀	0.623	0.548	0.94	0.358	0.85

$C'_M = 2.030$ mM						
C_B	w	E'	E_1	$\varphi_{R1} \times 10^3$	E_2	$\varphi_{R2} \times 10^3$
0.050	1.55 ₄	0.582	0.519	0.78	0.360	0.84
0.100	1.51 ₃	0.580	0.480	1.38	0.460	1.14
0.800	1.43 ₁	0.585	0.420	2.75	0.657	1.86
3.60	1.47 ₂	0.592	0.499	1.27	0.370	0.91

on its surface only, and that this part is easily washed away and does not enter into the calculation of φ_{R2} . The adsorption seems to be more pronounced at those ligand concentrations where the neutral complex is formed to a large part.

It is of interest to note that the φ_{R1} -values determined for $C'_M = 2.52$ mM are all smaller than those corresponding to $C'_M = 2.11$ mM.

Although the effect is small it is concordant with the surface adsorption analogue of the criterion on complex formation by the resin put forward by Fronæus ⁷, *i.e.*, the smaller C'_M is the higher will φ be.

It is also observed that the functions φ_R and φ_S exhibit maxima at almost the same value of C_B . This may, however, be fortuitous; the ion-exchange measurements should be regarded as the significant ones. The position of the

Table 4. The cyclohexanone-2-octanol extractions.

$C'_M = 2.111 \text{ mM}; \quad d = 2 \text{ cm}; \quad \epsilon_{510} = 2.82 \times 10^2$						
$\frac{C'_B}{M}$	$\frac{C_B}{M}$	E_3	$\frac{C_M}{\text{mM}}$	q	$\frac{C_{MS}}{\text{mM}}$	φ_S
0.050	0.049	0.568	1.17	1	0.95	0.81
0.100	0.096	0.504	1.03	1	1.08	1.04
0.400	0.370	0.435	0.89	1	1.22	1.37
0.800	0.715	0.466	0.80	1	1.31	1.65
1.200	1.04	0.369	0.76	1.01	1.35	1.79
1.500	1.28	0.403	0.83	1.02	1.28	1.55
1.800	1.51	0.445	0.91	1.04	1.19	1.31
2.400	1.96	0.496	1.02	1.18	1.09	1.07
3.60	2.79	0.596	1.22	2.51	0.99	0.81

maximum in the extraction case may depend on factors such as the mutual solubility of the solvents and the extraction of NH_4SCN into the organic phase.

MEASUREMENTS AT CONSTANT IONIC STRENGTH

Method and Formulae

In 3 M NaClO_4 the solubility of $\text{Co en}_2(\text{SCN})_2\text{ClO}_4$ is rather low (0.6 mM). Hence there is a possibility of studying the complex formation by solubility measurements.

The following notations are used

$$\beta_n = \frac{[\text{MB}_n]}{[\text{M}][\text{B}]^n} \quad (11)$$

$$X = \sum_{n=1}^n \beta_n [\text{B}]^n \quad (12)$$

$$L = [\text{M}][\text{C}] \quad (13)$$

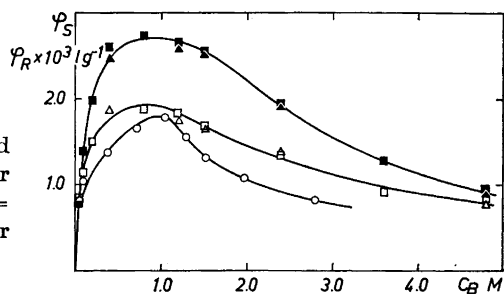


Fig. 2. The distribution quotients φ_R and φ_S . φ_{R1} for $C'_M = 2.52 \text{ mM}$ (\blacktriangle); φ_{R1} for $C'_M = 2.11$ or 2.03 mM (\blacksquare); φ_{R2} for $C'_M = 2.52 \text{ mM}$ (\triangle) and φ_{R2} for $C'_M = 2.11$ or 2.03 mM (\square). φ_S is marked by (\circ).

In eqn (13) the abbreviation C stands for ClO_4^- . This notation will be used throughout this paper. We then have

$$C_M = [M](1 + X) \quad (14)$$

From eqns (13) and (14) we obtain

$$1 + X = C_M \cdot [C]/L \quad (15)$$

$$\text{Now} \quad L = [M]_0[C]_0 = (C_M)_0[C]_0 \quad (16)$$

where indices mean $C_B = 0$. Thus

$$1 + X = \frac{C_M \cdot [C]}{(C_M)_0[C]_0} \quad (17)$$

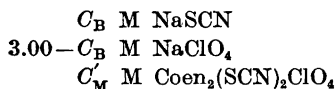
In the following the approximations $[B] = C_B$ and $[C] = C_C$ will be used, because of the small value of C_M . Hence, by measuring C_M , we can obtain X as a function of C_B . If the coefficients of activity of the ionic species concerned could have been regarded as constant we might have been able to calculate β_1, β_2, \dots by conventional methods. However, as the complexity is very weak it was necessary to use large ligand concentrations and thus the salt medium is changed to such a degree as to invalidate the supposition of constant activity coefficients.

The best we can hope for then is to be able to calculate β_1 from

$$\beta_1 = \lim_{C_B \rightarrow 0} \left(\frac{C_M \cdot C_C}{(C_M)_0 \cdot (C_C)_0} - 1 \right) \cdot \frac{1}{C_B} \quad (18)$$

Measurements

Procedure. Solutions of the composition



were shaken in the same black-painted bottles as before. After some time a precipitation of $\text{Co en}_2(\text{SCN})_2\text{ClO}_4$ was formed. From time to time samples of the solutions were withdrawn with a filterstick of fine porosity and were analyzed as before by measurement of the optical density at $510 \text{ m}\mu$ using the Hilger instrument and 2 cm quartz cells.

Chemicals used. Sodium perchlorate was prepared from analytical grade sodium carbonate and perchloric acid. Sodium thiocyanate was of analytical grade. The stock solutions were checked by ion-exchange-alkalimetric titration and Volhard titration, respectively.

Results

Unfortunately, equilibrium was very slowly reached. Experiments where solid $\text{Co en}_2(\text{SCN})_2\text{ClO}_4$ was added in excess to solutions of the above composition did not give reproducible results. The probable explanation may be slow rearrangements in the solid phase.

Table 5. Solubility measurements: Optical densities of the saturated solutions ($d = 2$ cm; $\lambda = 510$ m μ). Calculation of X/C_B .

C_B M	E					1 + X	X/C_B
	259 h	427 h	619 h	788 h	Mean		
0	0.354	0.345	0.340	0.339	0.345		0.30
0.3	0.428	0.419	0.418	0.411	0.419	1.093	0.31
0.43	0.472	0.459	0.456	0.451	0.459	1.140	0.33
0.60	0.520	0.511	0.510	0.507	0.512	1.187	0.31
0.90	0.645	0.637	0.639	0.635	0.639	1.297	0.33
1.20	0.835	0.822	0.819	0.815	0.823	1.431	0.36

$\beta_1 = 0.30 \pm 0.03$ M⁻¹

In Table 5 are given the results of a representative set of experiments, the precipitation formed from the supersaturated solutions with $C'_M = 3.00$ mM.

The calculations have been performed on the mean of the determinations at the four different times reported. If the shaking had been further prolonged, the hydration of the complex might have caused undesirable effects. It must be observed, however, that this hydration, the velocity of which is very low at 20°C¹⁵, would cause an increase of solubility. Also a *cis-trans* isomerization¹⁵ would have the same effect. Furthermore, if X is calculated from any of the separate sets of solubilities we obtain, within the experimental errors, the same value of $\lim_{C_B \rightarrow 0} X/C_B$ as that reported here, *i.e.*, 0.30 M⁻¹.

SEARCH FOR PERCHLORATE COMPLEXES

For reasons put forward in the following discussion it was deemed necessary to investigate also the eventual formation of perchlorate complexes of $\text{Co en}_2(\text{SCN})_2^+$. As the sorption of $\text{Co en}_2(\text{SCN})_2\text{ClO}_4$ on a perchlorate-saturated anion exchange resin was too small to permit a reliable analysis, only the solvent extraction technique was used. In order not to base judgment on one set of measurements only, two different extracting solvents were used, *viz.*, the cyclohexanone-2-octanol mixture and in the second case acetophenone.

M e a s u r e m e n t s

The measurements were performed as in the thiocyanate extractions.

The *acetophenone* used was a Merck preparation of the "wasserhell" quality. It was used without further purification.

The NaClO_4 concentration of the aqueous phase was determined alkalimetrically *via* a cation exchange resin in the acid form.

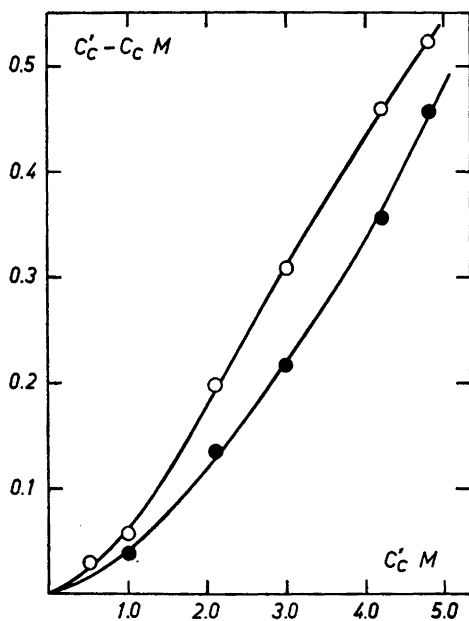


Fig. 3. Change of C_{NaClO_4} due to extraction. Cyclohexanone-2-octanol mixture (O); acetophenone (●).

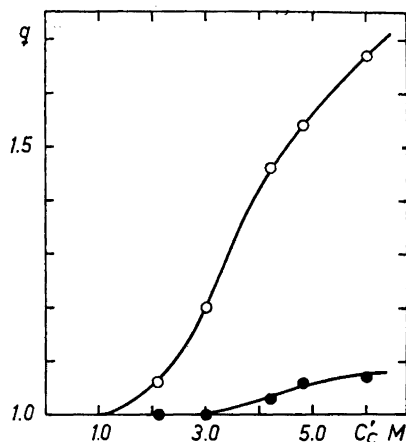


Fig. 4. Change of volume quotient q . Cyclohexanone-2-octanol mixture (O); acetophenone (●).

Results

The results are reported graphically only, as the calculations were very similar to those of the thiocyanate extractions. In Fig. 3 is given the decrease of sodium perchlorate concentration due to extraction into the organic phase. Fig. 4 shows the change in the volume quotient as the electrolyte concentration increases. Fig. 5 gives the final result. The quotient φ was reproducible to within about 1%. C'_M was kept low to avoid precipitation at the highest perchlorate concentrations.

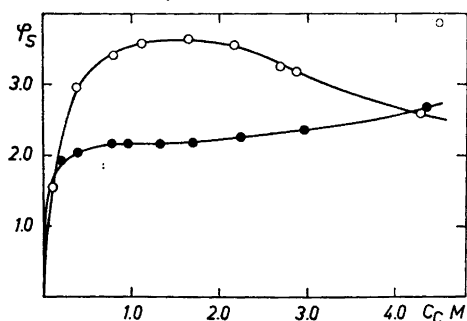


Fig. 5. Distribution quotient φ_s . Cyclohexanone-2-octanol mixture (O); acetophenone (●).

$C'_M = 0.5$ and 2 mM (*cyclohexanone-2-octanol*)

$C'_M = 2$ and 3 mM (*acetophenone*).

Only at $C'_C = 4.8$ M, $C'_M = 3$ mM was precipitation encountered. This point was then omitted.

DISCUSSION

If it is true, as infra-red data^{16,17} suggest, that hydrogen-bonding makes an important contribution to the effects causing outer-sphere complexity, then the relation between the complexity constants will depend almost exclusively on electrostatic and statistical factors. Thus if we start from the experimental value of β_1 , we can calculate the successive constants $\beta_2 \dots \beta_n$ from the statistical relation

$$\frac{b_{n+1}}{b_n} = \frac{(N-n)n}{(N-n+1)(n+1)} \quad (19)$$

where

$$b_n = \frac{\beta_n}{\beta_{n-1}} ; \quad b_1 = \beta_1 \quad (20)$$

given by Bjerrum (Ref.¹⁸, p. 24). These values must be maximum values, because of the neglect of the increasing electrostatic repulsion of negatively charged entities. In the present case, this neglect is certainly forgivable because we have chosen the large ions so as to minimize the electrical work.

In order to make use of eqn (19), we must make some assumption on the maximum coordination number N . It seems reasonable to assume that in this case $N = 8$, corresponding to the eight faces of an octahedron.

The calculation based on $\beta_1 = 0.3 \text{ M}^{-1}$ gave as result

$$\beta_2 = 0.04 \text{ M}^{-2}; \quad \beta_3 = 0.003 \text{ M}^{-3}; \quad \beta_4 = 0.0001 \text{ M}^{-4};$$

Then, from the well-known formula for \bar{n} (Ref.¹⁸, p. 21) we obtain for $[B] = 1 \text{ M}$ $\bar{n} = 0.28$, $\bar{n} = 0.29$ and $\bar{n} = 0.29$ if only the two, three and four first complexes are considered, respectively.

This result is in obvious variance with the result of the extraction experiments, which indicate, that $\bar{n} \approx 1$ when $[B] = 1 \text{ M}$.

Some of this disagreement certainly arises from the fact that we compare measurements made at different ionic strengths and in solutions of ammonium and sodium salts, respectively.

However, it seems to the present author that a rather probable explanation is that there might be a perchlorate complexity too, which is of a strength comparable in magnitude to the thiocyanate complexity.

If this is the case, it must be entirely wrong to compare results from measurements in a perchlorate-rich medium with such obtained in a perchlorate-free one.

In consequence of this assumption we must re-formulate the treatment of the solubility measurements.

The following notations are introduced:

$$\beta_{nB} = \frac{[MB_n]}{[M][B]^n} \quad (21a)$$

$$\beta_{nC} = \frac{[MC_n]}{[M][C]^n} \quad (21b)$$

meaning the "true" complexity constants in the sense of Leden (Ref.¹⁹, p. 40). We will assume in the following calculation that only the first two perchlorate complexes are formed in appreciable amounts. Then the only mixed complex to be considered is MBC, the complexity constant of which is defined as

$$\beta_{2BC} = \frac{[MBC]}{[M][B][C]} \quad (21c)$$

It may be assumed from energetical considerations that

$$2 \log \beta_{2BC} = \log \beta_{2B} + \log \beta_{2C} \quad (22)$$

or

$$\beta_{2BC} = \sqrt{\beta_{2B} \cdot \beta_{2C}} \quad (22a)$$

Hence eqn (14) turns into

$$C_M = [M](1 + X_B + X_C + \sqrt{\beta_{2B} \cdot \beta_{2C}} \cdot [B][C]) \quad (23)$$

Remembering that, in the actual case, $[B] + [C] = 3$, and combining eqn (23) with eqns (21) and (13) we obtain after trivial calculations

$$\begin{aligned} \frac{C_M \cdot [C]}{C_{M_0} \cdot [C]_0} = & 1 + \frac{\beta_{1B} - \beta_{1C} - 6\beta_{2C} + 3\sqrt{\beta_{2B} \cdot \beta_{2C}}}{1 + 3\beta_{1C} + 9\beta_{2C}} [B] + \\ & + \frac{\beta_{2B} + \beta_{2C} - \sqrt{\beta_{2B} \cdot \beta_{2C}}}{1 + 3\beta_{1C} + 9\beta_{2C}} [B]^2 + \frac{\beta_{3B}}{1 + 3\beta_{1C} + 9\beta_{2C}} [B]^3 + \dots \quad (24) \end{aligned}$$

Now the coefficient of the linear term of this expression must correspond to β_1 of eqn (18), *i.e.*, the experimentally determined quantity $\beta_1 = 0.3 \text{ M}^{-1}$. Thus we have

$$0.3(1 + 3\beta_{1C} + 9\beta_{2C}) = \beta_{1B} + 3\sqrt{\beta_{2C}} \cdot \sqrt{\beta_{2B}} - \beta_{1C} - 6\beta_{2C} \quad (25)$$

However,

$$\sqrt{\beta_{2B}} = \sqrt{\frac{b_2}{b_1}} \cdot \beta_{1B} \quad (26)$$

where $\frac{b_2}{b_1}$ is given by eqn (19).

Combining eqns (25) and (26) we finally obtain

$$\beta_{1B} = \frac{\beta_{1C} + 6\beta_{2C} + 0.3(1 + 3\beta_{1C} + 9\beta_{2C})}{1 + \frac{\sqrt{7}}{4} \sqrt{\beta_{2C}}} \quad (27)$$

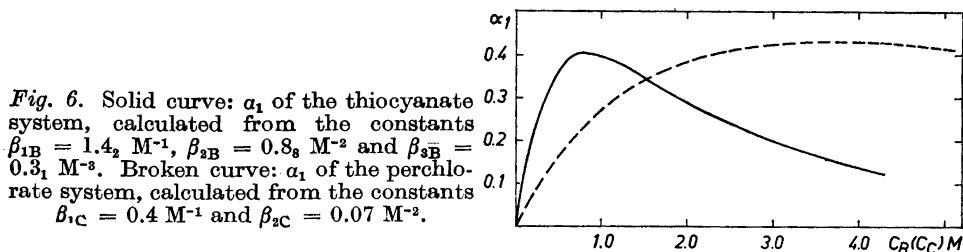


Fig. 6. Solid curve: α_1 of the thiocyanate system, calculated from the constants $\beta_{1B} = 1.4_2 \text{ M}^{-1}$, $\beta_{2B} = 0.8_8 \text{ M}^{-2}$ and $\beta_{3B} = 0.3_1 \text{ M}^{-3}$. Broken curve: α_1 of the perchlorate system, calculated from the constants $\beta_{1C} = 0.4 \text{ M}^{-1}$ and $\beta_{2C} = 0.07 \text{ M}^{-2}$.

From a value of β_{1B} one can calculate β_{2B} etc., from eqns (19) and (20).

We can then illustrate the interrelation of the thiocyanate and perchlorate complexity constants with a numerical example:

If we assume $\beta_{1C} = 0.4 \text{ M}^{-1}$, eqns (19) and (20) give $\beta_{2C} = 0.07 \text{ M}^{-2}$. Introducing these quantities in eqn (27) we obtain $\beta_{1B} = 1.4_2 \text{ M}^{-1}$. Hence $\beta_{2B} = 0.8_8 \text{ M}^{-2}$ and $\beta_{3B} = 0.3_1 \text{ M}^{-3}$. From these we may calculate \bar{n} for $[B] = 1 \text{ M}$.

Then we obtain $\bar{n} = 1.1_4$ if all three complexes are taken into account. Furthermore, a close examination of the φ_R -curves of Fig. 2 indicates that the maximum occurs at $C_B \approx 0.85 \text{ M}$. For this ligand concentration and the constants calculated above we obtain $\bar{n} = 1.0_1$.

Indeed, we can calculate α_1 for any concentration (Fig. 6). This quantity ⁷ is directly related to φ_R , and the agreement between the two quantities is very good. (At low concentrations the constants derived here are no longer valid, but should be greater so as to give a steeper rise of φ_R , which is actually found.)

As the curves of activity coefficients for NaClO_4 and NaSCN (Ref.²⁰) have rather broad minima in the region 1–3 M the variation of the value of the complexity constants with ionic strength may be negligible, which has been assumed above.

It is certainly not necessary to stress the arbitrary points in the above calculations. The purpose has been only to illustrate the composite problems encountered in the investigations of systems of such an elusively weak complexity.

The extraction experiments in perchlorate solutions were undertaken in an effort to prove the existence of perchlorate complexes. The results are, however, disappointing in this respect.

As these experiments are not a major part of the present investigation only the following may be said:

With systems where the mutual solubility of the two phases is as great as here one might expect large changes in the activity coefficients. These changes make any interpretation of the results very difficult. Reference might be made to the findings of Johnson and Brubaker ²¹ that cyclohexanone seems to enhance any tendency of anionic complex formation that may exist in the aqueous phase.

Comparison of Figs. 3 and 4 shows that it is not so much the extraction of NaClO_4 as the difference in mutual solubility (represented by different q) that causes the different shapes of the φ -curves.

It is interesting to note that if we calculate α_1 from the values of the complexity constants used above, $\beta_{1c} = 0.4 \text{ M}^{-1}$ and $\beta_{2c} = 0.07 \text{ M}^{-2}$, a very flat maximum is obtained at $C_c = 3.8 \text{ M}$; cf. Fig. 6. (Apart from activity effects causing changes in the parameters involved, α_1 should be related to φ_s in the same way⁷ as it is to φ_R .)

Summing up, we may state that there seems to be a definite tendency of thiocyanate ions associating with the *trans*-Co en₂(SCN)₂⁺ ion, and that the measurements can be correlated semi-quantatively on the basis of the hypothesis of a slight perchlorate complexity of this ion.

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