A STUDY OF THE CADMIUM THIOCYANATE COMPLEXES WITH A SILVER - SILVER THIOCYANATE ELECTRODE



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Master of Science.

by Peter Letkeman, B.Sc.(Hons.)

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ABSTRACT

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Abstract

The potential of a Ag - Ag(CNS) electrode vs. a saturated calomel was determined for a series of thiocyanate solutions ranging from 0.001 M - 0.100 M. These solutions with total metalion concentrations varying from 0.025 M to 0.25 M, were used to measure the degree of metal-thiocyanate complex formation. All solutions were kept at a constant ionic strength of 0.50, adjusted with sodium perchlorate. Essentially a new application of the e.m.f. method (The determination of formation constants from free ligand concentration data, rather than from free metal concentration data previously used) was introduced for the further investigation of metal-thiocyanate complexes at relatively low ligand concentrations. The formation constants of the first two cadmium complexes were determined to be 27.5 and 105 respectively.

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INTRODUCTION

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INTRODUCTION

Although the thiocyanate complexes of cadmium (7,10) and beryllium have been known for some years, only fragmentary studies have been made on their formation constants. Leden (16), in Germany, determined the formation constants of the first three mononuclear complexes of cadmium thiocyanate by measuring the free metal concentration with e.m.f. measurements and obtained $K_1 = 24.5$, $K_2 = 96$, and $K_3 = 380$ where the cumulative formation constant is defined by:

 $K_x = Cd (CNS)_x^{2-x}$

[Cd+][CNS]*

based on the equation $Cd^{++} + xCNS \rightleftharpoons Cd(CNS)_x^{2-x}$

Hume, Deford and Cave (II) were able to determine the formation constants of four thiocyanate complexes of cadmium with a polarographic technique by measuring the free metal concentration. Their values are $K_1 = 11.5$, $K_2 = 56$, $K_3 = 6$, $K_{l_4} = 60$, considerably different from those obtained by Leden.

Golub and Bilyk (15) studied the cadmium thiocyanate complexes with spectrophotometric and potentiometric methods, and postulated three species similar to those determined in Leden's work. They reported that at low concentrations only $Cd(CNS)^+$ was present. From 0.22 M thiocyanate to I.0.M, $Cd(CNS)_2$ was the complex formed and at higher concentrations $Cd(CNS)_3^$ was the predominant species present.

The formation constants obtained by the three independent groups are at a substantial dissagreement, thus meriting additional investigations in order to attempt a reconciliation of the conflicting data. R. Bock (5) who has done a considerable amount of research on the extractability of metal thiocyanates into ethyl ether, reported that beryllium was extracted into the organic layer when the aquenous phase contains a thiocyanate concentration above 1.00 M. He stated that 92% extraction was obtained at 7.00 M thiocyanate. The extraction of metals into organic liquids with suitable ligands (ie. CNS, Cl, NH₃, etc.) present, is explained in part by the fact, that the neutral metal complexes formed under the conditions described, show a preference to discolve in the organic solvent rather than in the aqueous phase. This ^{fe} solubility" or metal extraction into organic solvents, is a function of the complex, the ligand (pH at times) and the type of organic molecule present. A survey of the literature revealed that no one had reported the formation constant of beryllium thiocyanate, assuming the complex did exist.

In view of these facts, an investigation of the formation constants of the beryllium and cadmium thiocyanate complexes at low thiocyanate concentrations was undertaken.

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OBJECT

OBJECT

The object of this investigation was to obtain the formation constants of beryllium and cadmium thiocyanate complexes at a relatively low concentrations of thiocyanate. After considering the methods available, it was decided that the e.m.f. method using the Ag - Ag (CNS) electrode would be the most convenient and for the following reasons:

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- I. Reversible electrodes were available for the low concentration work.
- 2. The apparatus was relatively easy to assemble and would be of use for further investigation of thiocyanate complexes.
- 3. Since formation constants of cadmium complexes based on free metal concentration measurements were in some disagreement, free ligand concentration measurements would be a completely independent criterion to use in evaluating the formation constants.

EXPERIMENTAL

EXPERIMENTAL

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Materials

Throughout the work conductivity water, freshly distilled and collected near its boiling point, was used for the preparation of all solutions, all final washings and rinsings of electrode cells, pipettes, and other purposes related to the work.

Reagent Grade potassium thiocyanate, beryllium nitrate, cadmium nitrate, ammonium nitrate, sodium perchlorate and perchloric acid were used in the investigation without further purification. The potassium thiocyanate was dried in an oven at 130° C.

All solutions were made up on a moles per liter basis, and are in error, by synthesis, no more than I part in 1000. The error is estimated from; weighing of salts to within $^+0.2$ mg. and using 50 ml. pipettes with an accuracy of $^+$ 0.04 ml. Errors of this magnitude would contribute less than 0.04 mv. to the potential of the cell, seeing that a ten-fold change in thiocyanate concentration is equal to 60 mv. in the change of the cell's potential.

The silver oxide used to prepare the silver-silver thiocyanate electrodes was purified by R. Yamansaki. (26)

Apparatus

The water thermostat bath ($16^{n}L$, $13^{n}W$, $15^{n}D$) was controlled at $25^{\circ}C$ by a mercury regulator which was connected with a conventional triode relay circuit to a powerstat controlled heater. Effective circulation of the water was maintained by having a stirrer housed within the heating coil unit. Temperature control was maintained with $\pm.01^{\circ}$ of $25.0^{\circ}C$ as shown by temperature measurements taken with a Leeds and Northrup, type 8160, platinum resistance thermometer standardized by the manufacturer and compared to a second thermometer calibrated by the National Research Council (Canada). For this purpose a Mueller bridge made by the Rubicon Company was used. It was standardized with a Rubicon one ohm No. 56294 standard resistance coil.

The electrical measuring system consisted of a calibrated Rubicon Type B potentiometer, (with errors in potential no greater than 0.01%) a Leeds and Northrup Type E galvanometer with a sensitivity of $4.6 \ge 10^{-7}$ amp. mm.⁻¹, and an Eppley standard cell with an e.m.f. of 1.01936 volts. The Eppley cell was of the unsaturated, low resistance type with a negligible temperature coefficient. The entire system, including the water bath, was carefully grounded and shielded against stray potentials. The reference electrode was a Photovolt saturated calomel, Catalogue No. 1105.

Method

A cell was constructed using a silver-silver thiocyanate electrode and a saturated calomel as a reference electrode. A diagram of the electrode vessel is shown in figure 1.

Although the silver-silver halide electrodes have been the subject of many investigations, the silver-silver thiocyante electrode has received little attention. In the early 1900's some studies (1,6,13,14,17) were aimed at the evaluation of the solubility product of silver thiocyanate; later investigations by Pearce and Smith (19) and Aditya and Prasad (2) sought to determine the E^o value for the electrode. Recently (1956) Vanderzee and Smith (24) at the University of Nebraska have made a careful study of the thermal electrolytic type (12) electrode, and it was

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The General Setup.

PLATE I

- 6 -



The Electrode Vessel raised out of the constant temperature bath.

PLATE II

essentially their procedure that was followed in the preparation of the Ag-Ag (CNS) electrodes.

Solutions of potassium thiocyanate ranging from 0.00IM to 0.2M were prepared by adding a weighted amount of salt to distilled water and adjusting the ionic strength to 0.5 with sodium perchlorate. Similarly a series of cadmium and beryllium nitrate solutions were prepared ranging from 0.025M to 0.25M. A saturated ammonium nitrate solution was used in the electrode vessel to provide electrical contact between the calomel and silver-silver thiocyanate electrodes. The potential arising at the ammonium nitrate solution-thiocyanate solution junction was considered to be constant, due to a steady salt background (ionic strength at 0.50) and relatively small changes in the composition of the thiocyanate solution. The liquid junction potential (when steady) is unimportant where only the differences of e.m.f. readings are used to calculate the free thiocyanate concentrations.

The potentials of the thiocyanate solutions were measured against that of a saturated calomel. These measurements were repeated with six different electrodes and all agreed to within 0.3 mv. The e.m.f. values were plotted against the log of the thiocyanate concentrations on a large graph (scale of Imm.=C.2 mv.) and this graph is shown on a reduced scale in fugre 2. Several points on the graph were redetermined every week and found to be reproducible within 0.3 mv.

Vanderzee and Smith (24), Pearce and Smith (19), and Aditya and Prasad (2) have reported the E° value of the Ag-Ag(CNS) electrode at 25°C to be 0.08949, 0.0947, and 0.0878 volts respectively. In our investigation it was found that $E^{\circ} = 0.0940$ volts when any liquid junction potential was neglected and an estimated activity coefficient of

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Fig. I. The electrode vessel illustrating two Ag-Ag(CNS) electrodes (B) and a saturated calomel (A).

0.770 for a 0.10 M KCNS solution (the activity coefficient used is that for KCl, see ref. 26) was used in the Nernst equation. The potential of the saturated calomel was taken to be 0.2415 volts (26) in calculating the E° value. The potential of a saturated calomel is not quite agreed upon among different researchers (varying from 0.240 to 0.262 volts) and this could account for our E° value being high compared to those determined by Vanderzee (24) and Aditya (2) who employed a hydrogen electrode in their research.

The resulting e.m.f. of a solution containing an equimolar volume of metal to thiocyanate was recorded (Tables 2-6) and used to read directly from the graph (Fig. 2) the free thiocyanate concentration.

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TABLE 1

E.M.F. (Ag - Ag (CNS) electrode vs. calomel) for various concentrations of KCNS.

SCN⁻

E.M.F.

moles/liter x 10 ³	volts x 104
100.0	+ 785.0
90.0	755.0
80.0	725.0
75.0	714.0
60.0	653.0
50.0	605.0
40.0	545.0
30.0	473.0
25.0	428.0
20.0	367.0
10.0	190.0
9•0	158.0
8.0	129.0
7.0	95.0
6.0	55.0
5.0	10.0
4.0	- 50.0
3.0	120.0
2.0	225.0
1.0	435.0
0.75	482.0

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Preparation and Behaviour of the Ag-Ag(CNS) Electrodes

A platinum wire spiral, 1 cm. long and 3 mm. in diameter, one end mounted in soft glass tubing, was packed with a paste of pure silver oxide (26), dried in an oven for 5 hours at $425 - 450^{\circ}$ C and allowed to cool overnight. This left a layer of white shiny silver on the platinum spiral. This silver base was then made the anode in a solution, 0.20 M with respect to potassium thiocyanate and 0.06 M in perchloric acid. A current of 0.4 to 0.7 milliamperes was passed through this solution for a period of one hour. Electrodes were allowed to equilibrate in a portion of cell solution for 3 days before use. They normally reached equilibrium values in a day, showing little change in potential after the first 12 hours.

The electrodes prepared in this manner are generally gray in color; although occasionally one would be quite dark, it would show no difference in potential or behaviour. The electrodes were made up in groups of five. Any one electrode differing from the mean value by more than 0.3 mv. was discarded. After the initial equilibrating period, the electrodes were found to adjust to the changes in concentration (CNS⁻) quite rapidly; constant e.m.f. values were reached in 15 to 20 minutes.

THEORETICAL DISCUSSION

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Theoretical Discussion

In recent years, an increasing amount of interest has been shown in the problems associated with the formation of complex ions in aqueous solutions. In a classical review, Bjerrum (4) has pointed out that the formation of complexes always appears to occur in stepwise fashion, with the stabilities of the various complexes MA_j , characterized by a series of formation constants K_j , K_j .

There are available only a limited number of general mathematical methods for the calculation of successive formation constants, although a variety of slight modifications and specific applications of these general formulations have been made by a number of investigators. The three general treatments found in the literature are those by Leden (16), Bjerrum (3), and Fronaeus (9). The theory of calculating formation constants from experimental data, in an abbreviated form, is given below.

Symbols

 C_M = total metal concentration in moles per liter. (M)= free (unbound) metal ion concentration in moles per liter. C_A = total ligand concentration in moles per liter. (A)= free (unbound) ligand concentration in moles per liter. MA_n = concentration of complex in moles per liter.

n = any integral value from 1 to N.

- N = the number of ligands bound to the highest complex, i.e. the largest number of ligands bound to a complex.
- K = the formation constant (Law of Mass Action). The stoichiometric formation constant of the mononuclear complexes, MAn , $(0 \le n \le N)$ formed from the central metal ion, M,

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 $K = MA_n$ (M) (A)ⁿ

where charges are omitted for clarity.

The total metal concentration is given by:

or
$$C_{M} = M + MA + MA_{2} + MA_{3} + \dots MA_{N}$$

or $C_{M} = M + \sum_{l}^{\mu} K_{n}M(A)^{n} = \sum_{o}^{\mu} K_{n}(M)(A)^{n}$ (2)

and the total ligand concentration is given by a similar equation:

 $C_A = A + MA + 2MA_2 + 3 MA_3 + \dots N MA_N$

hence

$$C_{A} = (A) + \sum_{m \in I}^{m \in N} nK_{n} (M) (A)^{n}$$
(3)

The degree of formation of the system, or ligand number, \bar{n} , may be defined as the average number of ligands combined with each central group or metal ion.

Thus:
$$n = C_A - (A)$$

 C_M (4)

Then it follows from equations (2) and (3) that

ñ

$$= \sum_{m=1}^{m=N} n K_{n} (A)^{n}$$

$$\sum_{m=0}^{m=N} K_{n} (A)^{n} (5)$$

 $\sum_{m=0}^{m=N} (\bar{n} - n) \quad K_n (A)^n = 0 \tag{6}$

On rearranging equation (6) one obtains the general formula below:

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or

$$\frac{\bar{n}}{(L - \bar{n}(A))} = K_1 + K_2 \frac{(2 - \bar{n})}{(1 - \bar{n})} (A) + \sum_{m=3}^{m=N} \frac{(n - \bar{n})}{(1 - \bar{n})} K_n(A)^{n-1}$$
(7)

In any experiment, the total concentrations G_M and C_A , of metal and ligand will be known and, in principle, the determination of at least N values of the concentration of one of the complexes is sufficient for the computation of the formation constants. A set of values for \bar{n} and (A), when substitued into equation (7), will yield the formation constants. The equation itself (7) may, however become very difficult to solve when three or more complexes are formed in the same system. The value of \bar{n} is calculated from equation (μ), and (A) may be obtained experimentally in a variety of ways, i.e. from e.m.f. measurements, spectrophotometrically, solubility methods, from distribution coefficients, etc.

In order to test for the possible presence of polynuclear complexes, measurements were made at a number of C_M values. That is to say, if a polynuclear complex M_pA_n (p > I) is present, the formation constants calculated from equation (7) will vary with the different metal concentrations used. Similarly, if \bar{n} is a function of both (A) and C_M , at least one polynuclear complex is present, and the formation constants cannot be calculated by the conventional methods, unless the data can be extrapolated to low metal concentrations at which polynuclear complexes can be neglected (23). If no polynuclear complexes are formed, n is a function of (A) only, and is independent of $C_{M^{\circ}}$. This fact provides a simple test for presence of polynuclear complexes, namely, a plot of \bar{n} against (A) will yield a smooth curve for all mononuclear complexes, and separated curves for data containing any polynuclear complexes.

In the case where the first two complexes can be detected, and the higher complexes are neglected (because of the very small quantity present), equation (7) points out that a plot of $\frac{n}{(I - \bar{n})(A)}$ against $\frac{(2 - \bar{n})(A)}{(I - \bar{n})}$ yields a straight line of intercept K_{I} and a

of $K_{2^{\circ}}$ The above consideration is a special case of Rossotti's method (21) for the determination of formation constants. The above procedure was used in our investigation for the following reasons:

- (a) Hume and Leden (references 11 and 16) both reported that only Cd(CNS)⁺ and Cd(CNS)₂ could be detected below 0.30 M thiocyanate.
- (b) When a special case of Rossotti's method (given above)
 was applied to our data, a straight line plot was obtained,
 providing confirmatory evidence for the existance of only
 Cd(CNS)⁺ and Cd(CNS)₂ at low ligand concentrations.

Watkins and Jones (25) have recently shown that a relaxation method can be applied mathematically to a series of linear equations, containing K's, \underline{n} and (A), to obtain the various K values. They have demonstrated the method by recalculating numerous equilibrium constants from the published data by Leden (16), Hume (11) and Bjerrum (3). The table given below indicates the agreement between various K's calculated by the different investigators.

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Author	Complex	Kl	К2	K3	к ₄
Leden		57	220	2100	5000
	$Cd(Br)_n$				
Watkins + Jones		57	220	2000	6000
Bjerrum		235	6.45x10 ⁴	2.04x107	2.88x10
Watkins + Jones	$Zn(NH_3)_n$	250	8.0x10 ⁴	2.0x107	3.0x10 ⁹
Hume		11	56	6	60
Watkins + Jones	Cd(CNS) _n	8	58	8	58

The relaxation method can be applied in the calculation of successive stability constants in conjunction with the most commonly used experimental methods. It has the advantage of being capable of giving answers even in systems where large numbers of complexes are present and, in fact, it is here that it's advantages are seen most forcibly. The ease with which the method can be used in the solution of linear algebraic equations with large numbers of unknowns is an advantage over graphical methods. The method is superior to the use of determinants in the respect that it is an approximation

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method and in the respect that any number of equations equal to or greater than the number of unknowns can be used. In working with more equations than unknowns, poor data will not relax as far as good data when the majority of the data is relaxed and this gives an indication of the most suitable points. From these considerations and the example cited above, it is obvious that the relaxation method is best applied to systems of three and more complexes, where the determination of successive K's is rather difficult by graphical or conventional approximation methods.

The relaxation method has the disadvantage, characteristic of most algebraic methods, of treating the equations as exact and is not as flexible as graphical methods in allowing poor data to be selected and discarded. The results obtained are in good agreement with those obtained by other methods.

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RESULTS

Results

In Tables 2 - 6 are given the experimentally determined molar concentrations of free ligand (A), along with the calculated values of \bar{n} , etc. The assumption that any change in potential of the Ag-Ag(CNS) electrodes is due entirely to complex formation is implicit in the interpretation of the data. This assumption was felt to be valid because any variation in the liquid junction potential between the sodium perchlorate - thiocyanate mixture and saturated ammonium nitrate would be insignificant at low thiocyanate concentrations (20).

A thorough investigation of beryllium thiocyanate solutions revealed no complex formation that could be measured accurately by the e.m.f. technique. From the data (Table 2) recorded at 0.10M (CNS) concentrations it can be estimated that K_1 for Be(CNS)_x is less than 0.8, if it does form under the conditions described. At a thiocyanate concentration of 0.30M a substantial difference in voltage (2 mv.) was observed, along with some fluctuations in potential due to the increased formation of Ag(CNS)⁻⁷/₂ off the electrodes. The electrodes used at this high a concentration (0.30M CNS-) had to be replaced within two days of use, and hence the data obtained from those runs was discarded.

The cadmium thiocyanate solutions, on the other hand, did show moderate complex formation. The formation constants of the mononuclear cadmium thiocyanate complexes were determined graphically by Rossotti's method (example see Fig. 4 & 5) for all four sets of data (Tables 3 - 6), and are given below.

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the slope equal to K_2 .

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TABLE 2

Experimental Data and Related Quantities for Beryllium - Thiocyanate Solutions.

КŢ	=	Be($Be(CNS)^{+}$			
_		(Be ⁺	+)(CNS	•		

e.m.f.

	Car	C,	(A)	Къ
volts x 104	M	A		ـل محمد محمد محمد محمد مع
428.0 605.0 714.0 785.0	0.025M .025 .025 .025	0.025M .050 .075 .100	0.025M .050 .075 .100	- - -
605.0 775.0 880.0 955.0	0.050M .050 .050 .050	0.050M .100 .150 .200	0.050M .096 .1145 .195	0.8 0.4 0.5
605.0 785.0 960.0	0.100M .100 .100	0.050M .100 .200	0.050M .100 .197	0.3
785.0 955.0 1050.0	0.30M .30 .30	0.100M .200 .300	0.100M .195 .285	0.2 0.1
780•0 955•0 1050•0	0.50M .50 .50	.100M .200 .300	0.098 .195 .285	0.05 0.05 0.10

Note:

A change of 0.5 mv. in the potential changes K_1 by .4, hence the the K_1 values given have very little meaning, considering that the potential is obtained with an accuracy of $\frac{+}{-}$ p.3 mv.

1999 - 1999 1999 - 1999 1999 - 1999

- 26 -TABLE 3

Experimental data and Related Quantities for 0.25M Cd. solutions.

Note:

concentrations of solutions given inmoles/litre, e.m.f. is the potential of Ag-Ag(SCN) electrode vs. calomel.

e.m.f.						
volts x 10 ⁴	C <u>A</u>	(A)	n	$\frac{n}{(l-n)(A)}$	<u>(2-n (A)</u> 1-n)	
+ 325.0	0.100M	0.017M	•330	29.2	•0424	
240.0	. 075	. 0125	. 250	26.5	•029l	
124.0	•050	•007 7	.170	26.4	•0170	
- 69.0	• 025	•0036	•085	26.0	.0075	
255.0	•0125	•0018	.043	25.0	•0037	
440.0	•00625	•0009	.021	24.2	.0018	
545.0	•0040	•00059	•014	23.6	.0012	: : :

TABLE 4

Experimental data and Related quantities for 0.10M Cd solutions.

e.m.f. volts x 10 ⁴	C _A	(A)	n	<u>n</u> (1-n) (A)	(2-n) (A) 1-n)	
+ 540.0	0.100M	0.039M	0.610	40.1	.1390	
1,145.0	•075	•027	. 480	34.2	•0789	
318.0	• 050	.0165	•335	30.5	.0410	-șt.
121.0	. 025	.0 076	.174	27.8	.01 68	
- 80.0	.0125	. 0034	.091	26.9	.0072	ц.
262.0	. 00625	.00173	•045	26.3	•0035	
425.0	•0040	.00110	. 029	26.2	•0022	

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TABLE 5

e.m.f. ñ CA (A) $\frac{\overline{n}}{(1-n)(A)}$ $\frac{(2-\bar{n})(A)}{(1-n)}$ volts x 10^{4} + 653.0 0.100M0.060M .800 66.0 .3600 518.0 .075 .640 .043 41.3 .1630 435.0 •050 .026 •486 35.5 .0890 235.0 .025 .012 .260 29.2 .0280 35.0 .0125 •0055 .140 29.6 .0120 - 150.0 .00625 .00265 .072 29.3 .0055 262.0 .0040 .00170 •046 28.4 .0035

Experimental data and Related quantities for 0.05M Cd solutions.

TABLE 6

Experimental data and Related quantities for 0.025M Cd Solutions

e.m.f.		/ \				and the second secon
volts x 10^{4}	C	(A)	n	$\frac{n}{(1-\bar{n})}$	(2-n)(A) (1 - n)	
+ 720.0	0.100M	0.078M	. 880	91.2	.5100	
635.0	•075	• 056	•760	56.4	. 2890	
513.0	. 050	• 035	•600	42.8	.1230	
310.0	。 025	.016	•360	35.4	•0410	
118.0	.0125	.0076	.196	32.0	.0170	
65.0	.00625	.0037	.102	30.7	•0078	
- 180.0	•007to	.0024	•064	29. 5	.0050	

Metal Concentration	КŢ	K ₂	in Charlen and a start that the second s
0.25 M Cd	24.5	115	
O.lO M Cd	2 6 . 0	102	
0.05 M Cd	28.0	98	
0.025 M Cd	30.0	105	
Average K & deviation	27 . 5 ^{±3}	105 ± 10	

A plot of \bar{n} vs. (A) as a test (21) for polynuclear complex formation is given in figure 3. To within expermental error no polynuclear species seem to be present, for the points fall on a smooth curve going through the origin. If any polynuclear complexes were present one would find the points of different metal concentration data giving parallel curves (22), the spparation of the curves indicating the degree of polynuclear complex formation.

CONCLUSION

Conclusion

The formation constants obtained in our investigation are of the same magnitude as those determined by Leden (16), but vary by a factor of two when compared with the work of Hume (11) or Golub and Bilyk (15). Hume (11), and his coworkers, reported that the formation constants determined under variable ionic strength showed a deviation of ± 5 for K₁, and ± 15 for K₂. The methods of calculating the formation constants (graphical, approximations, relaxation, etc.) can cause a deviation as large as $\pm 25\%$ of the K values, as shown in the chapter on Theoretical Discussion. In view of these possible differences in the K values determined among the various investigators, our results compare very well with those obtained by Leden (16), as seen in the chart below.

	<u>к</u> т	^K 2	
Author	27.5	105	
Leden	24.5	96	
Hume	11.5	56	
G olu b	80.0	175	

The disagreement with the formation constants determined by Hume and Golub is not so great when their experimental conditions and basic assumptions are carefully examined. Golub and Bilyk (15) postulated that only $Cd(CNS)^+$ was formed below 0.22 M (CNS⁻). This postulation is contrary to the interpretation of the data given by Leden (16), Hume (11) and our investigation. If, however, our data is conditioned to Golub's assumption, a K₁ value of approximately 70 is obtained for a thiocyanate concentration up to 0.10 M. This K₁ would be larger (≈ 100) if data up to 0.20 M (CNS⁻) were available, seeing there is a steady increase in

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 K_1 with an increase in thiocyanate concentration (see Tables 3 - 6). Hume (11), in his investigation, used a range of thiocyanate concentrated trations from 0.10 M to 2.00 M. With these relatively more concentrated solutions he was examining the third and fourth complexes carefully, while only a small portion of the ligand concentration was bound up in Cd(CNS)⁺ and Cd(CNS)₂. It is evident that his K_1 and K_2 values are apt to be in substantial error, because his procedure favored the formation of the higher complexes. With the above considerations in mind, the apparent contradiction in the formation constants determined by the various researchers is really abolished, and the deviations are within the possible errors encountered in the experimental and theoretical procedures.

A surey of the chart on page 28 reveals a gradual increase in K_1 (24.5 - 30.0) with a decrease in cadmium concentration. The possible errors in our K values, taking into account e.m.f. readings, mixing of solutions and graphical treatment of the data, is $\pm 10\%$ for K_1 and $\pm 20\%$ for K_2 . The gradual increase in K_1 values, which is in the range of experimental error, could possibly show the presence of small amounts of the third cadmium complex Cd(CNS) $\frac{1}{3}$. The Cd(CNS) $\frac{1}{3}$ complex, if present below 0.10 M (CNS⁻), is negligible as far as the theoretical calculation for K_1 and K_2 is concerned. For if substantial quantities of Cd(CNS) $\frac{1}{3}$ had been present, the data would not have yielded a straight line plot as shown in figure 4 and 5. In our investigation then, only Cd(CNS)⁺ and Cd(CNS) could be detected experimentally below a tenth molar thiosyanate concentration.

The extraction of cadmium, from aqueous thiosyanate solutions, with organic solvents can be correlated with the normal extraction of

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metal thiogyanate complexes. The extraction of beryllium under similar conditions is not simply the extraction of the complex, for the formation constant (≈ 0.5) of Be(CNS)⁺ could not account for 90% extraction reported by Bock (5). The determination of the beryllium thiogyanate formation constants at relatively high thiogyanate concentrations is inevitable before any explanation for high beryllium extraction will be possible.

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