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The Complex Formation in the Zinc Thiosulfate and the Cadmium Thiosulfate Systems

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The complex formation in the zinc thiosulfate and the cadmium thiosulfate systems in aqueous solution has been studied by potentiometric measurements with amalgam electrodes. The measurements were performed at 25.0°C and the ionic strength 3.0 M using sodium perchlorate as ionic medium. The following overall stability constants were obtained.

For zinc: $\beta_1 = (9.2 \pm 0.3)$ M^{-1}; $\beta_2 = (88 \pm 4)$ M^{-2}
$\beta_3 = (2.00 \pm 0.02) \times 10^3$ M^{-3}; $\beta_{42} = (6.9 \pm 1) \times 10^5$ M^{-5}

For cadmium: $\beta_1 = (5.5 \pm 0.4) \times 10^2$ M^{-1}; $\beta_2 = (4.5 \pm 0.6) \times 10^4$ M^{-2}
$\beta_3 = (9.0 \pm 0.2) \times 10^6$ M^{-3}; $\beta_4 = (1.32 \pm 0.06) \times 10^7$ M^{-4}
$\beta_{42} = (1.5 \pm 0.3) \times 10^{11}$ M^{-5}

(The stated errors are 99.9 % confidence limits.)

Several investigations have been performed concerning the kind and the strength of the complexes formed in aqueous solutions by zinc and cadmium ions with thiosulfate ions.[1-3] As early as 1904 Euler published results from potentiometric measurements with metal electrodes.[4] He reported the complex formation between zinc ions and thiosulfate ions to be so weak that no stability constants could be calculated from his measurements. For the cadmium thiosulfate system he noticed a considerably stronger complex formation. His results give a value of the overall stability constant of the fourth mononuclear complex, $\beta_4 = 3 \times 10^7$ M^{-4}. Since the work of Euler, several other authors have studied these two systems using various methods. For the zinc thiosulfate system stability constants of the first two mononuclear complexes have been reported,[1,2] and Brinzinger and Eckardt [5] concluded on the basis of dialytic measurements that a third complex exists. The agreement between the values suggested for β_1 and especially for β_2 by different authors is, however, poor, and no value of β_3 seems to have been reported. The possible existence of a fourth mononuclear complex has not been confirmed.

The results of previous investigations of the cadmium thiosulfate system show a better agreement as far as the first two mononuclear complexes are concerned, and values of the stability constant of the third mononuclear

complex have also been reported.[1] The question whether a fourth complex may be formed or not still remains. Most of the investigations have been based on polarography. Surprisingly enough no potentiometric measurements using cadmium amalgam electrodes seem to have been reported so far.

The present work was done with the aim to further elucidate the complex formation in these two systems. Since the complexes could be expected to be comparatively weak, potentiometric measurement with metal amalgam electrodes was chosen as the method presumably best suited to give accurate results.

CALCULATIONS OF STABILITY CONSTANTS

The methods of calculation have been elaborated by Bjerrum,[6] Leden,[7] and Fronæus.[8] The symbols, if not otherwise defined, are those proposed by Fronæus.[8]

I. Only mononuclear complexes are formed. The cumulative stability constant β_n is defined from the equation:

$$\beta_n = \frac{[MA_n]}{[M][A]^n} \qquad n = 0, 1, 2 \cdots N \tag{1}$$

$$E_M = E - E_0 = \frac{RT}{\nu F} \ln X \tag{2}$$

The ligand number $\bar{n}$ may be expressed as

$$\bar{n} = \sum_{i=1}^{N} i\beta_i[A]^i / \sum_{i=0}^{N} \beta_i[A]^i \tag{3}$$

and also in the form

$$\bar{n} = \frac{\nu F}{RT} \frac{dE_M}{d \ln [A]} \tag{4}$$

Graphical determination. The graphical determination of stability constants of the mononuclear complexes was carried out in the way described by Fronæus (Ref. 8, p. 18).

Numerical calculations. The experimental results have also been treated numerically using a program elaborated by Sandell.[9] This program is designed for calculation of stability constants for weak complex systems by a computer and is based upon the same principles as the graphical method, *i.e.* cutting C_A, E_M curves at certain E_M values and extrapolation of $C_A = f(C_M)$ to $C_M = 0$.

Description of the experiments by means of the stability constants. When a set of stability constants has been calculated it is important to check how close the constants describe the experimental results. In such a check it is desirable to use primarily measured variables for which the random errors can be easily estimated. In the case of potentiometric central ion measurements it seems convenient to choose (C_A, E_M) values for checking.

A direct comparison with the experimental (C_A, E_M) values can be made by use of the equation

$$[A]=C_A/(1+C_M\cdot X'/X) \quad (5)$$

Starting with the stability constants calculated and experimental values of C_A and C_M, a corresponding value of [A] can be obtained from iterative calculations using eqn. (5) and beginning with the approximation $[A]\approx C_A$. The iteration can for instance be based upon the method of Newton-Raphson (*vide, e.g.*, Ref. 18). X can then be calculated and finally E_M from eqn. (2). The differences $(E_M)_{exp}-(E_M)_{calc}$ can now be compared to the experimental errors expected.

If the experimental E_M and the corresponding value calculated from the stability constants differ more than can be explained by the random experimental errors, the discrepancy can of course depend on several reasons. Adjusting the stability constants originally calculated might give a better description; the experimental errors may be larger than expected; diffusion potentials and ionic medium changes may influence, and there is also the possibility that further species are formed, *e.g.* polynuclear complexes. The kind and magnitude of the differences between experimental and calculated values of E_M indicates whether further treatment of the data is necessary.

II. Mononuclear and dinuclear complexes are formed. If both mononuclear and dinuclear complexes exist the total concentration of metal ion and ligand, respectively, will be given by

$$C_M=[M]+\sum_{i=1}^{N}[MA_i]+2\sum_{k=1}^{L}[M_2A_k] \quad (6)$$

and

$$C_A=[A]+\sum_{i=1}^{N}i[MA_i]+\sum_{k=1}^{L}k[M_2A_k] \quad (7)$$

The cumulative stability constant for the dinuclear complex M_2A_k is defined from

$$\beta_{k2}=\frac{[M_2A_k]}{[M]^2[A]^k} \quad (8)$$

A plot of C_A as a function of C_M at constant E_M will not give a straight line in this case since

$$E_M=\frac{RT}{\nu F}\ln(X+2[M]Y) \quad (9)$$

where

$$Y=\sum_{k=1}^{L}\beta_{k2}[A]^k \quad (10)$$

and [A] will not be constant at constant E_M. Also here, however, extrapolation to $C_M=0$ will give corresponding values of X and [A], and the stability constants of the mononuclear complexes can be calculated as before. From eqn. (9) it is clear that a constant value of E_M will cause a constant value of $X+2[M]Y$. Then the following equation may be derived

$$\lim_{C_M \to 0} \left(\frac{\partial C_A}{\partial C_M} \right)_{E_M} = k_0 = \bar{n}_I - \frac{2Y}{XX'} \tag{11}$$

When the stability constants of the mononuclear complexes have been calculated, eqn. (11) may be used for estimation of the dinuclear complex formation as proposed by Fronæus.[8] The method is limited by the difficulties of obtaining accurate values of k_0. As a complement, the following method has been used in the present investigations to study the stability of dinuclear complexes. The function Y may be expressed as

$$Y = \left(\frac{C_M}{[M]} - X \right) / 2[M] \tag{12}$$

By use of the experimental values of C_A, C_M, and E_M and the stability constants for the mononuclear complexes, Y can be calculated from eqn. (12). [M] is obtained directly from the emf measured. A primary value of [A] is computed from C_A, C_M, and β_i (eqn. (5)) and then X is obtained from β_i and [A]. The functions $Y/[A]^k$ are now plotted against [A] for successive values of k until an origin intercept $\neq 0$ is obtained giving a primary value of β_{k2}. The slope for $[A]=0$ is a measure of $\beta_{(k+1)2}$. Further treatment is analogous to that outlined for the mononuclear complexes. Of course only those parts of the series should be used where the experimental values of E_M differ substantially from those calculated from the mononuclear complexes. Better values of the stability constants for the dinuclear complexes may be calculated by iteration in the following way. The primary values of β_{k2} are introduced in eqn. (7), which is then solved for [A]. These values of [A] are used to recalculate Y from eqn. (12), and the new functions $Y/[A]^k$ are plotted against [A]. If only one dinuclear complex is formed, the corresponding term may be eliminated between (6) and (7), which gives an equation from which [A] can be solved since the stability constants for the mononuclear complexes are known.

EXPERIMENTAL

Chemicals

Zinc perchlorate was prepared from freshly heated zinc oxide (Merck *p.a.*) and perchloric acid (Baker *p.a.*).

Cadmium perchlorate was prepared from cadmium oxide (Baker *p.a.*) and perchloric acid (Baker *p.a.*).

Sodium perchlorate was prepared in two different ways. In the case of the zinc thiosulfate system, sodium carbonate (Merck *p.a.*), and perchloric acid (Baker *p.a.*) were used. The solution was rendered acid, boiled for half an hour and then neutralized with carbonate-free sodium hydroxide. After three days it was filtered. The filtrate was boiled until a skin was formed on the surface and then filtered again at about 115°C. In the case of the cadmium thiosulfate system commercial sodium perchlorate (Fluka *p.a.*) was dissolved in distilled water, allowed to stand for a few days, and then filtered through a 0.45 μ Millipore filter.

The amount of protolytic substances was checked in both cases by potentiometric titrations with a glass electrode and was found to correspond to less than 10^{-5} mol H^+ per mol sodium perchlorate.

Sodium thiosulphate was Merck *p.a.* The solution was standardized against potassium dichromate (Merck *p.a.*).

Zinc: Merck *p.a.*, washed with dilute sulphuric acid.

Cadmium: Baker *p.a.*, washed with dilute sulphuric acid.

Mercury: Merck *p.a.*

Zinc amalgam was prepared by a slight modification of the method described by Sillén and Liljekvist [10] (Fig. 1). Zinc amalgam is very sensitive towards oxidation, and

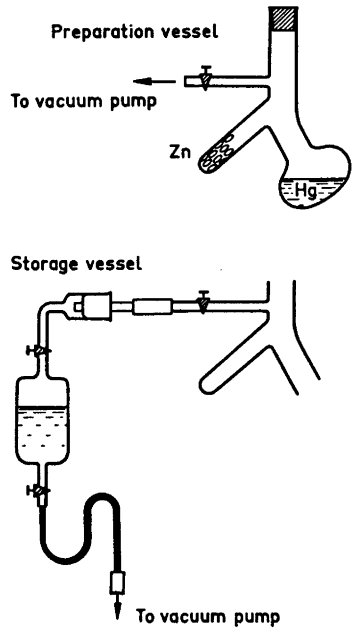

Fig. 1. Preparation of amalgam.

air must be excluded from the amalgam. After evacuation of the preparation vessel the zinc pellets were brought into the mercury and kept there at 60°C for 24 h. Then the storage vessel was evacuated and the amalgam transferred into it. The amalgam was stored under nitrogen. The amount of zinc was 2.5 % by weight resulting in a two-phase amalgam. All stopcocks were fitted with teflon plugs. The amalgam prepared in this way functioned perfectly.

Cadmium amalgam was prepared exactly as zinc amalgam and here a two-phase amalgam containing 8 % cadmium was used.

Measurements

The emf E of a galvanic cell of the following composition was measured. (M = Zn and Cd, respectively.)

−					+
M (Hg)	C_M C_A $3M-3(C_M+C_A)$	$M(ClO_4)_2$ $Na_2S_2O_3$ $NaClO_4$	3.00 M $NaClO_4$	10 mM NaCl 2.99 M $NaClO_4$	Ag,AgCl(s)

The reference electrode was prepared according to Brown.[11] The electrode solution was saturated with silver chloride. Oxygen was excluded from the titration solutions by

using a special titration vessel (type Ingold) with a tight fitting lid and capillary outlet tubes. The solution in the left-hand half cell was prepared by adding a volume v of a solution T to a volume V_0 of a solution S.

$$\text{S: } \begin{cases} C_M & M(ClO_4)_2 \\ 3M - 3C_M & NaClO_4 \end{cases} \qquad \text{T: } \begin{cases} C_M & M(ClO_4)_2 \\ C_A^0 & Na_2S_2O_3 \\ 3M - 3(C_M + C_A^0) & NaClO_4 \end{cases}$$

In the measurements $V_0 = 20.00$ ml and the temperature 25.00 ± 0.05°C. Before the amalgam was added, a stream of nitrogen was bubbled through the solutions S and T to remove oxygen. Traces of oxygen in the nitrogen gas were removed by leading the gas through a furnace with activated Cu.[12] The nitrogen was then bubbled through 3.00 M $NaClO_4$ to attain the correct vapor pressure before passing through the titration vessel, where it also caused the mixing of the solutions. The nitrogen stream was used for agitating the amalgam as well, so that a fresh surface was always maintained.

In the case of the zinc thiosulfate system, a Norma potentiometer was used provided with a Kipp Light Spot Galvanometer as zero instrument (accuracy 0.01 mV). The solution T was added with a 10 ml piston burette (Metrohm E 274). In the cadmium thiosulfate measurements a digital voltmeter (DM 2022) was used (accuracy 0.01 mV in the actual range). To obtain good accuracy over the whole ligand concentration range, the titrations were divided into two series for every C_M. The first series was performed with $C_A^0 = 200$ mM. The solution T was added from an all-glass syringe outfit with a specially made micrometer screw. In the second series C_A^0 was 800 mM and a 20 ml piston burette was used for T.

All titration series were repeated at least once and the reproducibility was in general within 0.2 mV in the zinc thiosulfate system and within 0.3 mV in the cadmium thiosulfate system.

The choice of pH in the solutions is important. Below pH ≈ 4 the thiosulfate decomposes, and somewhat above pH = 5 the hydrolysis of the metal ions is no longer negligible. The pH was adjusted by addition of $HClO_4$ to somewhat below 4.5 for the solution S and to about 4.5 for T. In the case of the cadmium thiosulfate system, fresh solutions and a careful adjustment of pH turned out to be necessary to avoid the formation of a yellow precipitate, probably CdS, that occurred at elevated pH values, and also when the solutions were allowed to stand for a few days.

RESULTS

The zinc thiosulfate system. At first the validity of the equation

$$E = E^0 - \frac{RT}{2F} \ln [M] \tag{13}$$

for the cell used was checked by titrations without ligand and found to be satisfied within ± 0.1 mV for 1 mM $\leq [Zn^{2+}] \leq 70$ mM and pH ≈ 3.

The titration series were performed with $C_M = 2.02$ mM, 10.10 mM and 20.20 mM, respectively. The value of E_0 for each series was determined by graphical extrapolations of $E = f(C_A)$ to $C_A = 0$. Some values of C_A and E_M from the titration series are collected in Table 1. The data were treated numerically according to Sandell [9] and the following stability constants were obtained for the mononuclear complexes.

$$\beta_1 = 9.20 \pm 0.26 \text{ M}^{-1}$$
$$\beta_2 = 87.5 \pm 4.0 \text{ M}^{-2}$$
$$\beta_3 = 1998 \pm 14 \text{ M}^{-3}$$

(The stated errors are 99.9 % confidence limits.)

Table 1. Corresponding values of C_A and E_M for the zinc thiosulfate system. E_M' has been calculated from the stability constants of the mononuclear complexes and E_M'' considering also a dinuclear complex. C_A in mM and E_M in mV.
$\Delta E_M' = E_M - E_M'$; $\Delta E_M'' = E_M - E_M''$.

$C_M = 2.02$ mM				$C_M = 10.10$ mM				$C_M = 20.20$ mM			
C_A	E_M	$\Delta E_M'$	$\Delta E_M''$	C_A	E_M	$\Delta E_M'$	$\Delta E_M''$	C_A	E_M	$\Delta E_M'$	$\Delta E_M''$
19.6	2.8	0.2	0.2	19.4	2.3	0.0	0.0	19.2	2.2	0.1	0.2
43.0	6.7	0.0	0.0	33.5	4.3	0.0	0.0	37.7	4.6	0.3	0.2
60.9	10.5	0.1	0.0	47.1	6.5	0.1	−0.1	51.1	6.6	0.5	0.3
73.9	13.5	0.2	0.1	60.4	9.1	0.3	0.1	68.4	9.3	0.7	0.3
86.6	16.3	0.1	−0.1	73.3	11.4	0.3	−0.1	80.9	11.2	0.7	0.1
98.9	19.3	0.3	0.1	85.9	14.0	0.4	−0.1	93.1	13.1	0.6	−0.2
110.9	22.1	0.3	0.2	98.1	16.5	0.5	−0.1	108.9	16.4	1.2	0.2
122.6	24.6	0.3	0.1	110.0	19.0	0.6	−0.1	120.4	18.4	1.2	0.0
133.9	27.0	0.3	0.1	121.6	21.3	0.5	−0.2	131.5	20.6	1.4	0.1
145.0	29.2	0.2	0.0	132.9	23.7	0.6	−0.1	142.4	22.6	1.4	0.1
159.3	32.0	0.2	0.0	143.8	25.7	0.4	−0.3	153.0	24.6	1.5	0.1
173.2	34.5	0.1	0.0	154.6	28.0	0.6	−0.1	166.7	26.9	1.3	−0.1
186.6	37.0	0.2	0.1	165.0	30.1	0.7	0.0	180.0	29.3	1.3	−0.1
199.6	39.2	0.2	0.1	181.8	33.2	0.7	0.0	196.0	32.1	1.3	−0.1
215.3	41.6	0.1	0.0	198.0	36.0	0.7	0.0	211.4	34.7	1.3	−0.1
230.3	44.0	0.2	0.1	213.5	38.6	0.7	0.1	226.2	37.1	1.2	−0.1
244.8	46.0	0.1	0.0	228.5	41.1	0.8	0.2	240.4	39.3	1.1	−0.1
258.7	48.0	0.2	0.1	256.7	44.9	0.4	−0.1	254.1	41.4	1.1	0.0
277.4	50.4	0.1	0.0	275.2	47.4	0.3	−0.2	272.4	44.1	1.1	0.0
297.6	53.0	0.2	0.1	292.8	49.6	0.1	−0.3	289.9	46.5	1.0	0.1
314.4	54.9	0.1	0.1	307.2	51.4	0.1	−0.2	304.1	48.4	1.0	0.1
332.7	57.0	0.2	0.1	330.0	54.1	0.1	−0.2	326.7	51.1	0.8	0.0
354.1	59.1	0.0	0.0	351.3	56.5	0.1	−0.1	347.7	53.6	0.8	0.0
374.3	61.4	0.3	0.2	371.3	58.7	0.2	−0.2	367.5	55.8	0.7	0.0
402	64.0	0.3	0.2	399.0	61.4	0.1	−0.1	394.9	58.6	0.6	0.0
428	66.3	0.3	0.2	424	63.8	0.1	−0.1	420	61.1	0.5	0.0
459	68.9	0.3	0.3	448	65.9	0.2	0.0	443	63.4	0.6	0.2
499	72.2	0.4	0.4	469	67.8	0.2	0.1	490	67.6	0.7	0.3
534	74.7	0.4	0.4	495	69.9	0.2	0.1	554	72.6	0.7	0.3
564	76.8	0.5	0.4	530	72.7	0.4	0.3	588	75.1	0.7	0.4

A graphical calculation gave a set of constants that agreed very closely with those from the numerical calculations. The function X_2 represented a straight line and accordingly X_3 gave constant values over the whole ligand range investigated. Thus no indication of a fourth mononuclear complex could be discovered. Another check was made by measurements at high ligand concentrations (0.6 M − 1.5 M) and calculations of $\bar{n}$ from eqn. (4) (the Bodländer equation). These calculations gave $\bar{n} = 2.8 - 3.0$, further strengthening the assumption of three mononuclear complexes. Values of E_M' were now obtained from the stability constants of the mononuclear complexes as described above. The differences between the experimental and the calculated values of E_M are given in Table 1.

This comparison shows a deviation between experimental and calculated E_M at moderate values of C_A that is much larger than can be explained by errors in the measurements. The difference is monotonously increasing with C_M, thus indicating the presence of polynuclear complexes. An investigation using eqn. (11) and plotting successive functions $Y/[A]^k$ indicated the formation of one dinuclear complex, $Zn_2(S_2O_3)_4^{4-}$. From the series with $C_M = 10.10$ and 20.20 mM a value of the stability constant β_{42} could be obtained from values of Y, calculated from eqn. (12)

$$2Zn^{2+} + 4S_2O_3^{2-} \rightleftharpoons Zn_2(S_2O_3)_4^{4-} \quad \beta_{42} = (6.9 \pm 1) \times 10^5 \text{ M}^{-5}$$

E_M'' was computed from the values of the stability constants of mononuclear and dinuclear complexes and compared to the experimental values of E_M (Table 1). These calculations were performed with the aid of Sandell's[9] data program using eqns. (6), (7), and (9). The deviations were entirely within the expected experimental errors.

In Fig. 2 $\bar{n}$, calculated from eqn. (3), is represented as a function of log[A].

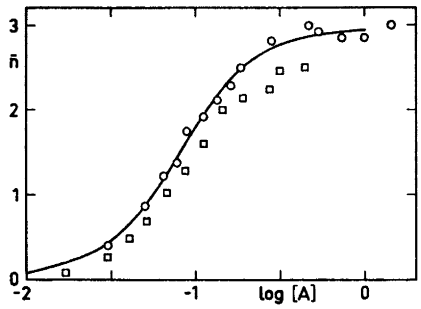

Fig. 2. The complex formation curve for the zinc-thiosulfate system. The full-drawn curve represents $\bar{n}_I$, calculated from eqn. (3). $\bar{n}_I$ calculated from eqn. (4) is denoted by O, and k_0 from the slope of the C_A,C_M-curves by □. ([A] in M.)

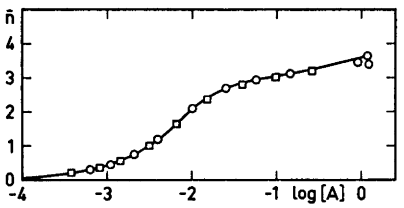

Fig. 3. The complex formation curve for the cadmium-thiosulfate system. The full-drawn curve represents $\bar{n}_I$, calculated from eqn. (3). $\bar{n}_I$ calculated from eqn. (4) is denoted by O, and k_0 from the slope of the C_A,C_M-curves by □. ([A] in M.)

A check must now be made that two possible sources of error, namely hydrolysis of the metal ion and the existence of $HS_2O_3^-$, do not appreciably affect the experimental results. In the titrations pH has been kept at about 4.5. The influence of hydrolysis must be largest at small thiosulfate ion concentrations (about 20 mM in the present measurements). According to Schorsch,[13] the following two hydrolysis equilibria dominate in zinc salt solutions of not too high pH values.

$$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+ \qquad \log K_{11} = -9.25$$

$$2Zn^{2+} + H_2O \rightleftharpoons Zn_2OH^{3+} + H^+ \qquad \log K_{12} = -7.50$$

The medium used was 3 M NaCl and the temperature 25.0°C. An estimation of the error due to hydrolysis using these constants gives

$$\frac{[ZnOH^+]}{[ZnS_2O_3]} < 10^{-3} \text{ and } \frac{[Zn_2OH^{3+}]}{[ZnS_2O_3]} < 10^{-3}$$

A similar discussion based on the hydrolysis constants proposed by Sekine [14] gives also the result that the amount of hydrolysis products is negligible. A determination of the dissociation constants of $H_2S_2O_3$ has been carried out by Page,[15] who found $pK_1 \approx 0.3$ and $pK_2 \approx 1$, which gives $[HS_2O_3^-]/[S_2O_3^{2-}] = 3 \times 10^{-4}$ at pH = 4.5. The fraction of thiosulfate existing as $HS_2O_3^-$ is apparently negligible.

The cadmium thiosulfate system. The measurements were performed in the same way as described for the zinc thiosulfate system. Eqn. (13) was found to be valid within ± 0.1 mV for 2 mM $\leq [Cd^{2+}] \leq$ 40 mM. Four titration series were carried out with $C_M = 2.00$ mM, 5.00 mM, 10.00 mM, and 20.00 mM,

Table 2. Corresponding values of C_A and E_M for the cadmium thiosulfate system. E_M' has been calculated from the stability constants of the mononuclear complexes and E_M'' considering also a dinuclear complex. C_A in mM and E_M in mV.
$\Delta E_M' = E_M - E_M'$; $\Delta E_M'' = E_M - E_M''$.

$C_M = 2.00$ mM				$C_M = 5.00$ mM			
C_A	E_M	$\Delta E_M'$	$\Delta E_M''$	C_A	E_M	$\Delta E_M'$	$\Delta E_M''$
0.797	2.7	0.0	0.0	1.325	2.5	−0.1	−0.1
1.587	5.3	0.0	0.0	2.631	5.0	−0.2	−0.1
2.372	7.8	0.0	0.0	3.922	7.6	−0.2	−0.2
3.150	10.1	−0.1	−0.1	5.20	10.1	−0.2	−0.2
3.922	12.5	0.0	0.0	7.69	15.0	−0.1	−0.1
5.45	16.9	0.1	0.1	10.13	19.7	0.1	0.0
7.20	21.8	0.3	0.2	13.08	25.3	0.3	0.0
9.16	26.9	0.4	0.3	16.51	31.8	0.4	0.0
11.08	31.8	0.5	0.3	19.28	36.9	0.4	0.0
13.20	36.9	0.6	0.4	22.49	42.8	0.5	0.0
15.50	42.2	0.7	0.5	25.58	48.2	0.5	0.0
19.06	49.5	0.7	0.5	28.57	53.1	0.4	−0.1
23.11	56.8	0.7	0.5	31.46	57.6	0.4	0.0
27.78	64.0	0.5	0.4	36.07	64.1	0.2	−0.1
33.33	71.4	0.4	0.3	40.4	69.7	0.1	−0.2
39.57	78.5	0.4	0.3	46.2	76.1	0.0	−0.2
46.2	84.8	0.3	0.2	52.9	82.8	−0.1	−0.2
53.0	90.5	0.2	0.2	59.2	88.0	−0.2	−0.3
59.8	95.7	0.3	0.3	66.1	93.1	−0.4	−0.4
67.3	100.5	0.2	0.2	80.0	102.2	−0.3	−0.4
80.0	107.7	0.2	0.2	105.0	114.8	−0.2	−0.2
104.4	118.6	0.1	0.1	133.3	125.7	−0.1	−0.1
133.3	128.8	0.0	0.0	172.6	137.2	−0.1	−0.1
172.6	139.7	0.1	0.1	207.4	145.4	0.0	0.0
207.4	147.5	0.1	0.1	238.6	151.6	0.0	0.0
238.6	153.4	0.1	0.1	266.7	156.5	0.0	0.0
266.7	158.1	0.0	0.0	298.4	161.5	0.0	0.0
298.4	162.9	0.0	0.0	319.5	164.4	−0.1	−0.1
329.4	167.2	0.0	0.0	355.6	169.1	−0.2	−0.2
367.6	171.7	−0.3	−0.3	389.7	173.1	−0.3	−0.3

respectively. Reports of the hydrolysis of zinc ions [1,13,14] and of cadmium ions [1,16] indicate that the cadmium ions are less hydrolyzed than the zinc ions. Furthermore, in the cadmium thiosulfate titrations the acidity of the solution S was adjusted to be close to pH 4.0. Separately measured values of E_0 were used. Some values of C_A and E_M from the titration series are collected in Tables 2 and 3. Graphical and numerical calculations gave also here consistent results for the stability constants. The following set was obtained for the mononuclear complexes from the numerical calculations:

$$\beta_1 = (554 \pm 41)\ \mathrm{M}^{-1}$$
$$\beta_2 = (4.46 \pm 0.58) \times 10^4\ \mathrm{M}^{-2}$$
$$\beta_3 = (8.95 \pm 0.14) \times 10^6\ \mathrm{M}^{-3}$$
$$\beta_4 = (1.32 \pm 0.058) \times 10^7\ \mathrm{M}^{-4}$$

Table 3. Corresponding values of C_A and E_M for the cadmium thiosulfate system. E_M' has been calculated from the stability constants of the mononuclear complexes and E_M'' considering also a dinuclear complex. C_A in mM and E_M in mV.
$\Delta E_M' = E_M - E_M'$; $\Delta E_M'' = E_M - E_M''$.

$C_M = 10.00$ mM				$C_M = 20.00$ mM			
C_A	E_M	$\Delta E_M'$	$\Delta E_M''$	C_A	E_M	$\Delta E_M'$	$\Delta E_M''$
1.325	1.5	0.0	0.0	3.483	2.2	0.1	0.1
3.150	3.7	0.1	0.1	6.93	4.5	0.0	0.0
3.922	4.7	0.2	0.2	10.34	6.8	0.0	0.1
6.45	7.8	0.1	0.1	13.73	9.2	0.0	0.1
8.92	10.9	0.1	0.2	20.39	14.1	0.1	0.2
11.32	14.0	0.2	0.2	26.92	18.9	0.3	0.3
16.51	20.6	0.6	0.4	33.33	23.9	0.6	0.2
20.90	26.3	0.8	0.4	39.62	29.4	1.2	0.4
25.58	32.6	1.2	0.5	45.8	34.8	1.5	0.2
30.03	38.8	1.4	0.5	51.9	40.4	1.6	−0.2
35.17	46.0	1.4	0.3	57.8	46.4	1.9	−0.2
40.4	53.3	1.3	0.3	63.6	52.4	2.0	−0.2
45.4	59.9	1.1	0.2	69.4	58.4	1.7	−0.4
50.8	66.5	0.9	0.2	75.0	64.1	1.4	−0.4
57.1	73.6	0.8	0.2	83.3	72.5	1.2	−0.2
63.7	80.0	0.4	0.0	91.3	79.7	0.9	−0.1
70.7	86.1	0.3	0.0	99.1	86.1	0.7	−0.1
77.1	91.0	0.1	−0.1	106.8	91.6	0.4	−0.1
96.9	103.5	−0.1	−0.2	119.1	99.4	0.2	−0.1
120.8	115.2	−0.1	−0.1	133.2	107.1	0.2	−0.1
160.0	129.3	0.0	−0.1	146.6	113.4	0.2	0.0
196.2	139.4	0.2	0.2	169.7	122.4	0.1	0.0
228.6	146.7	0.2	0.2	192.8	129.9	0.1	0.0
257.6	152.3	0.2	0.2	217.2	136.6	0.0	0.0
287.2	157.3	0.1	0.1	246.9	143.5	−0.1	−0.1
319.5	162.2	0.0	0.0	288.2	151.9	0.1	0.1
355.6	167.0	−0.2	−0.2	321.6	157.6	0.1	0.1
389.7	171.1	−0.3	−0.3	368.2	164.3	−0.1	−0.1
409.8	173.6	−0.2	−0.2	408.3	169.3	−0.4	−0.3
436.4	176.3	−0.4	−0.4	440.7	173.0	−0.5	−0.5

(The stated errors are 99.9 % confidence limits.) As in the case of the zinc thiosulfate system, measurements at high ligand concentrations (0.8 M – 1.3 M) were performed in order to calculate $\bar{n}$ from the Bodländer equation (4). These calculations gave $\bar{n} = 3.4 - 3.7$, supporting the existence of a fourth mononuclear complex. From the stability constants of the mononuclear complexes E_M' was calculated as described in section I. The differences between the experimental and the calculated values of E_M are given in Tables 2 and 3, showing the same kind of deviation as in the zinc thiosulfate system. A consideration similar to that already described for zinc thiosulfate indicated the existence of the same type of dinuclear complex, *i.e.* $Cd_2(S_2O_3)_4^{4-}$,

$$2Cd^{2+} + 4S_2O_3^{2-} \rightleftharpoons Cd_2(S_2O_3)_4^{4-};\ \beta_{42} = (1.5 \pm 0.3) \times 10^{11}\ M^{-5}$$

E_M'' was also here calculated from the stability constants of mononuclear and dinuclear complexes. The deviations from the experimental values, shown in Tables 2 and 3, are within the expected experimental errors.

In Fig. 3 $\bar{n}$, calculated from eqn. (3), is represented as a function of log[A].

DISCUSSION

The potentiometric measurements on the zinc thiosulfate and the cadmium thiosulfate systems can be accounted for if it is assumed that there exist three mononuclear complexes and one dinuclear complex, $Zn_2(S_2O_3)_4^{4-}$, in the former system and four mononuclear and one dinuclear complex, $Cd_2(S_2O_3)_4^{4-}$, in the latter system. In both systems the second mononuclear complex is weak compared to the third complex which dominates over a large part of the ligand range.

The experiments cannot be described within the expected errors only by means of mononuclear complexes. The discrepancy arises at a rather small thiosulfate concentration and disappears at moderate ligand concentration. It is not very probable that the discrepancy is caused entirely by medium changes and diffusion potentials, especially as an ionic medium is used with high concentration of inert electrolyte (3.0 M $NaClO_4$).

With the assumption of a dinuclear complex M_2A_4 a good description of the experimental results is obtained. The maximum fraction of metal ion existing as a dinuclear complex at $C_M = 20$ mM has been calculated to about 10 – 12 % in both systems, permitting a reasonable accuracy in the determination of the corresponding stability constant.

The composition of the suggested dinuclear complex is interesting. Both metals apparently prefer three-coordination to thiosulfate ions in the case of mononuclear complexes, and the simplest dinuclear complex with three-coordinated metal atoms is in fact

Migal *et al.*[17] have investigated the cadmium thiosulfate system and found three mononuclear complexes, the stability constants of which agree very well with those obtained in the present investigation.

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