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

HANS PERSSON

Division of Physical Chemistry, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The formation of complexes in aqueous solution between cyanide ions and zinc and cadmium ions, respectively, has been studied by potentiometric measurements at 25.0°C and ionic strength 3.0 M using sodium perchlorate as ionic medium. The following overall stability constants were obtained (subjectively estimated maximum errors are given).

For the zinc cyanide system:

$\beta_1 = (2.2 \pm 0.5) \times 10^5$ M^{-1}; $\beta_2 = (1.06 \pm 0.06) \times 10^{11}$ M^{-2}
$\beta_3 = (4.8 \pm 0.5) \times 10^{16}$ M^{-3}; $\beta_4 = (3.7 \pm 0.8) \times 10^{21}$ M^{-4}

For the cadmium cyanide system:

$\beta_1 = (4.2 \pm 0.1) \times 10^5$ M^{-1}; $\beta_2 = (6.9 \pm 0.5) \times 10^{10}$ M^{-2}
$\beta_3 = (5.3 \pm 0.3) \times 10^{15}$ M^{-3}; $\beta_4 = (1.6 \pm 0.4) \times 10^{19}$ M^{-4}

The dissociation constant for hydrogen cyanide, the ionization constant for water, and the stoichiometric solubility product for zinc cyanide were also determined under the specified conditions.

Several investigations of the zinc cyanide and the cadmium cyanide systems using different methods have been made,[1,2] one of the most recent being the pH-measurements on the zinc cyanide system performed by Izatt *et al.*[2] These authors claim that the species $Zn(CN)_2$, $Zn(CN)_3^-$, and $Zn(CN)_4^{2-}$ exist and give the corresponding stability constants. They also report that no species $ZnCN^+$ seems to be formed in the solution. Izatt *et al.* point out that in most of the work done earlier on the zinc cyanide system, amalgam electrodes have been used, and that zinc amalgam has been reported to be attacked by cyanide ions. Amalgam measurements might thus give doubtful results. However, it seemed odd that the first complex could not be detected, and it also seemed reasonable that by careful exclusion of oxygen from the solutions and with a low concentration of cyanide ions, the amalgam method might still be successful, at least for determination of the first complexity constant.

Measurements on the zinc cyanide system were therefore performed with both an amalgam electrode and a glass electrode. The cadmium cyanide system, previously studied by Leden [8] with amalgam electrode measurements, was investigated with the aid of a glass electrode.

CALCULATIONS OF STABILITY CONSTANTS

The stability constants were determined with the method of graphical integration of $\bar{n}/[A]$, outlined by Fronæus (Ref. 3, p. 14). The concentration of free ligand A has been calculated from the equation

$$[A] = \frac{K_a(C_H + oh - h)}{h} \quad (1)$$

where K_a is the dissociation constant for hydrogen cyanide and C_H the total concentration of perchloric acid in the solution. The concentration of hydrogen ions, h, was calculated from measurements with a glass electrode according to the relation

$$E_H = E_H^0 - \frac{RT}{F} \ln h \quad (2)$$

$\bar{n}$ was obtained from

$$\bar{n} = (C_A - [A] - [HA])/C_M \quad (3)$$

An approximate value of β_1 was obtained from a combination of the amalgam measurements and the pH-measurements, the former giving values of the function X, and the latter giving the corresponding values of [A].*

EXPERIMENTAL

Chemicals

Perchloric acid, *sodium perchlorate*, *zinc amalgam*, *zinc perchlorate*, and *cadmium perchlorate* were as described in a previous paper.[4] *Sodium cyanide* was Baker's *p.a.* sample. It was analysed for cyanide by titration with a silver nitrate solution (Liebig titration). A titration with a standardized solution of perchloric acid showed that the sample contained a small amount of strong base, probably NaOH, that had to be considered in the calculations.

Measurements

The zinc cyanide system. Combined amalgam- and pH-measurements. The measurements on the zinc cyanide system were originally designed in the following way.

A volume V_0 of a solution S_1 was titrated with a solution T_1 (with volume v). ($V_0 = 25.00$ ml.)

$$S_1 \begin{cases} C_M & Zn(ClO_4)_2 \\ C_{HS} & HClO_4 \\ 3M - 3C_M & NaClO_4 \end{cases} \qquad T_1 \begin{cases} C_M & Zn(ClO_4)_2 \\ C_{HT} & HClO_4 \\ C_{AT} & NaCN \\ 3M - 3C_M - C_{AT} - C_{HT} & NaClO_4 \end{cases}$$

Here C_M, C_{AT}, and C_{HT} had values in the concentration ranges 0.5 – 1 mM, 20 – 100 mM, and 10 – 50 mM, respectively. The emf's of the following galvanic cells were measured:

I. Zn(Hg) | $S_1 + T_1$ | 3.00 M $NaClO_4$ | $\begin{matrix} 10 \text{ mM NaCl} \\ 2.99 \text{ M } NaClO_4 \end{matrix}$ | Ag, AgCl

II. Glass electrode | $S_1 + T_1$ | 3.00 M $NaClO_4$ | $\begin{matrix} 10 \text{ mM NaCl} \\ 2.99 \text{ M } NaClO_4 \end{matrix}$ | Ag, AgCl

* Symbols, if not else defined, are those used by Fronæus.[3]

In this way it was intended to determine both the free central ion concentration and the free ligand ion concentration. However, two difficulties arose in the course of the titrations. Firstly, a precipitation occurred when only a part of a titration series was performed, and secondly, analyses of solutions, before precipitation had occurred, showed that some zinc had been dissolved from the amalgam. The amount of zinc dissolved increased rapidly with the cyanide concentration. The solutions were analysed for zinc both polarographically and by EDTA-titrations. Hence, it was clear that the amalgam method could not be used in the broad range of cyanide concentrations. However, the simultaneous measurements of the free central ion concentration and the free ligand ion concentration gave corresponding values of the function X_1 and [A] at low ligand concentrations, thus providing an approximate value of β_1. Furthermore, measurements with precipitate present gave an approximate value of the stoichiometric solubility product for $Zn(CN)_2(s)$, $K_s = [Zn^{2+}][CN^-]^2$. (The precipitate was analysed and found to be $Zn(CN)_2$ in the ligand range studied.)

The zinc cyanide system. pH-measurements. Since the zinc amalgam electrode was proved unsuitable in cyanide-rich solutions, the investigations were continued as pure pH-measurements with a glass electrode. To avoid precipitation the titration series had to be performed with varying C_M, by titrating cyanide-rich zinc solutions with perchloric acid. The titration solutions were composed as follows.

$$S_2 \begin{cases} C_{MS} & Zn(ClO_4)_2 \\ C_{AS} & NaCN \\ C_{HS} & HClO_4 \\ 3M - 3C_{MS} - C_{AS} & NaClO_4 \end{cases} \qquad T_2 \begin{cases} C_{HT} & HClO_4 \\ 3M - C_{HT} & NaClO_4 \end{cases}$$

One series was also performed with constant C_M at such high ligand concentrations that no precipitation could be expected. Even when the titration series were performed in the way outlined above, precipitation occurred for some series in the range about $\bar{n} = 2$. The appearance of solid zinc cyanide in a series was immediately shown by a drift in the emf. If no precipitate was formed, the potential attained a stable value within a minute after an addition of titrant solution. To control if this drift really depended upon precipitation, titrant was added until the emf was stable again, *i.e.* until the precipitate had been dissolved. The values of ([A], $\bar{n}$) now calculated were, within the limits of experimental accuracy, the same as those for series where no precipitation had occurred. To avoid precipitation it was essential to use freshly prepared solutions.

The investigations on the *cadmium cyanide system* were carried out as pH-measurements exactly as described above for the zinc cyanide system. No precipitation of cadmium cyanide was obtained even when C_M was kept constant. In the zinc cyanide measurements the emf was measured with a Radiometer potentiometer pHM 4C and a Beckman glass electrode 40495. In the studies of the cadmium cyanide system an Orion digital voltmeter was used together with a Jena glass electrode HA 9401/21. The glass electrodes were checked against a hydrogen electrode. The Beckman electrode was found to follow the hydrogen electrode within 0.4 mV and the Jena electrode within 0.2 mV in the range $3 < -\log[H_3O^+] < 10.5$. The glass electrodes were calibrated in a buffer [30 mM NaAc, 30 mM HAc, 2.97 M $NaClO_4$] in which $-\log[H_3O^+] = 5.015$ according to previous measurements on the proton-acetate system.[5] The reproducibility of the measured emf in the titration series was in general within 1 mV.

Determination of K_w *and* K_a. A calculation of the free cyanide ion concentration also requires a value of the ionization constant for water, K_w, and the dissociation constant for hydrogen cyanide, K_a, in 3 M $NaClO_4$ and at 25°C. K_w was determined from measurements of the hydrogen ion concentration in a solution with known hydroxide ion concentration by means of a hydrogen electrode and K_a from measurements with a glass electrode in a solution ($S + T_3 + T_4$) produced by titrating a solution S:(3.00 M $NaClO_4$) with two solutions, T_3:(C_A NaCN, 3 M $- C_A$ $NaClO_4$), and T_4:(C_H $HClO_4$, 3 M $- C_H$ $NaClO_4$).

The following values were obtained from the measurements: $pK_w = 14.184 \pm 0.002$, and $pK_a = 9.484 \pm 0.01$. Ågren [6] has reported a value of $pK_w = 14.15 \pm 0.01$, and Ingri *et al.*[7] $pK_w = 14.22 \pm 0.02$.

RESULTS

The zinc cyanide system. pH-measurements. In Tables 1 and 2 some representative values of added volume of titrant and measured emf are collected.

Table 1. Corresponding values of added volume, v, of titrant and measured emf, E_H, for the zinc cyanide system (v in ml, and E_H in mV).

Series 1				Series 2			
$E_H^0 = -131.4$ mV $C_{MS} = 0.300$ mM; $C_{MT} = 0$ mM $C_{AS} = 1.530$ mM; $C_{AT} = 0$ mM $C_{HS} = 0.04$ mM; $C_{HT} = 3.030$ mM				$E_H^0 = -131.0$ mV $C_{MS} = 0.500$ mM; $C_{MT} = 0$ mM $C_{AS} = 3.066$ mM; $C_{AT} = 0$ mM $C_{HS} = 0.04$ mM; $C_{HT} = 6.06$ mM			
v	E_H	v	E_H	v	E_H	v	E_H
2.625	372.6	8.530	281.0	3.937	370.8	8.202	274.8
2.953	363.9	8.858	278.5	4.199	362.0	8.530	271.2
3.281	355.0	9.186	275.8	4.462	352.9	8.858	268.3
3.609	346.4	9.514	272.7	4.724	344.0	9.186	265.1
3.773	342.0	9.842	269.8	4.987	335.6	9.514	261.9
3.937	338.2	10.170	266.7	5.118	331.4	9.842	258.8
4.101	334.0	10.498	263.2	5.249	327.3	10.170	255.6
4.265	330.6	10.826	259.1	5.380	323.4	10.498	252.1
4.593	324.1	11.154	254.1	5.511	319.5	10.826	248.3
4.921	318.4	11.318	250.9	5.643	315.8	10.990	246.2
5.249	313.3	11.482	247.3	5.774	312.3	11.154	243.6
5.577	308.7	11.646	242.5	5.905	308.1	11.318	241.1
5.905	304.9	11.712	240.2	6.069	305.2	11.482	238.2
6.233	301.2	11.876	233.0	6.233	301.7	11.646	234.8
6.561	298.0	12.007	224.5	6.397	298.4	11.745	232.2
6.889	294.9	12.138	211.2	6.561	295.6	11.941	225.8
7.217	291.9	12.204	202.1	6.889	290.0	12.105	217.5
7.545	290.0	12.269	191.5	7.217	285.7	12.237	206.8
7.873	286.4	12.335	179.9	7.545	281.8	12.335	194.8
8.202	283.7	12.401	169.3	7.873	278.1	12.466	168.2

In order to get a realistic conception of the error limits, the calculations were performed in the following way. $\bar{n}/[A]$ was plotted as a function of [A] for the different series, and one upper and one lower limiting curve were then drawn. No variation of $\bar{n}/[A]$ with C_M could be detected. By graphical integrations and plots of successive X_i-functions [3] the corresponding two sets of stability constants were determined.

The following average values were obtained:

$$\beta_1 = (2.2 \pm 0.5) \times 10^5 \text{ M}^{-1}; \qquad \beta_2 = (1.06 \pm 0.06) \times 10^{11} \text{ M}^{-2}$$
$$\beta_3 = (4.8 \pm 0.5) \times 10^{16} \text{ M}^{-3}; \qquad \beta_4 = (3.7 \pm 0.8) \times 10^{21} \text{ M}^{-4}$$

The complex formation curve, $\bar{n}([A])$, calculated from the stability constants, is drawn in Fig. 1, and in the same diagram some experimental values are plotted.

Table 2. Corresponding values of added volume, v, of titrant and measured emf, E_H, for the zinc cyanide system. The second titration series was performed with constant $C_M = 1.017$ mM and without ligand in the titrant (v in ml, and E_H in mV).

Series 3						Series 4	
$E_H^0 = -127.4$ mV $C_{MS} = 0.304$ mM; $C_{MT} = 0$ mM $C_{AS} = 1.238$ mM; $C_{AT} = 0$ mM $C_{HS} = 0.02$ mM; $C_{HT} = 2.518$ mM						$E_H^0 = -119.2$ mV $C_{AS} = 10.03$ mM $C_{HS} = 0.01$ mM $C_{HT} = 20.21$ mM	
v	E_H	v	E_H	v	E_H	v	E_H
1.936	363.2	5.643	308.0	10.728	265.2	6.102	340.5
2.132	358.6	6.036	304.6	11.056	260.1	6.168	336.3
2.329	354.0	6.430	301.3	11.285	255.8	6.233	332.3
2.526	349.7	6.824	298.3	11.482	251.8	6.299	328.3
2.756	345.1	7.217	295.4	11.646	247.0	6.397	322.6
2.985	340.8	7.545	292.7	11.810	240.0	6.496	317.3
3.248	336.0	7.873	290.5	11.876	236.3	6.594	312.1
3.543	331.3	8.202	288.0	11.941	231.8	6.692	307.3
3.871	326.8	8.694	284.4	11.991	227.7	6.791	302.5
4.199	322.7	9.186	280.6			6.889	298.1
4.560	318.5	9.678	276.7			6.988	293.9
4.921	314.8	10.071	272.6			7.086	290.0
5.249	311.5	10.400	269.2			7.185	284.8

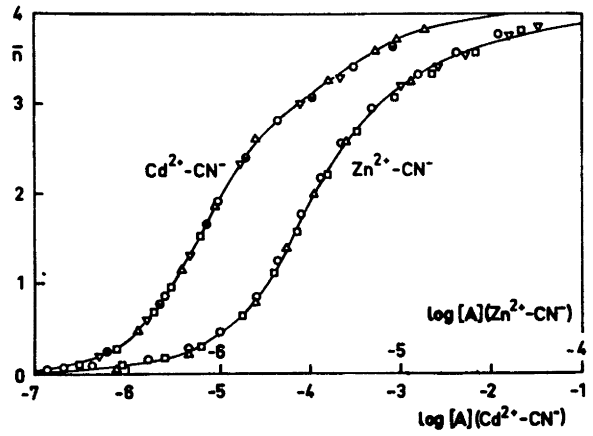

Fig. 1. The complex formation curves for the zinc and cadmium cyanide systems. The full-drawn curves represent $\bar{n}$ calculated from the stability constants. $\bar{n}$ calculated from eqn. (3) is denoted by ○ (series 1), □ (series 2), △ (series 3), and ▽ (series 4) for the zinc system; and by ○ (series 5), □ (series 6), △ (series 7), ▽ (series 8), and ◒ (series 9) for the cadmium system. ([A] in M.)

The zinc cyanide system. Combined amalgam- and pH-measurements. From the combined measurements of central ion and ligand concentrations ap-

proximative values of $\beta_1 = (3 \pm 1.5) \times 10^5$ M^{-1} and $K_s = (3.3 \pm 1.3) \times 10^{-16}$ M^{-3} were obtained.

The cadmium cyanide system. The stability constants for the cadmium cyanide system were calculated by analogy to the zinc cyanide system. The

Table 3. Corresponding values of added volume, v, of titrant and measured emf, E_H, for the cadmium cyanide system (v in ml, and E_H in mV).

Series 5				Series 6			
$E_H^0 = -514.9$ mV $C_{MS} = 1.000$ mM; $C_{MT} = 1.000$ mM $C_{AS} = 5.035$ mM; $C_{AT} = 0$ mM $C_{HS} = 0.11$ mM; $C_{HT} = 10.15$ mM				$E_H^0 = -511.7$ mV $C_{MS} = 1.000$ mM; $C_{MT} = 1.000$ mM $C_{AS} = 0$ mM; $C_{AT} = 10.00$ mM $C_{HS} = 0.15$ mM; $C_{HT} = 5.08$ mM			
v	E_H	v	E_H	v	$-E_H$	v	$-E_H$
2.156	17.8	6.468	−96.8	0.962	142.6	6.966	105.5
2.455	8.9	6.767	−101.1	1.095	137.8	7.297	104.9
2.853	4.2	7.065	−105.2	1.261	133.4	7.629	104.4
3.085	−12.4	7.364	−109.3	1.460	129.5	7.961	103.8
3.400	−24.2	7.662	−113.2	1.725	125.8	8.293	103.1
3.632	−33.0	7.977	−117.4	1.990	123.0	8.624	102.6
3.864	−41.2	8.293	−121.6	2.322	120.3	8.956	102.1
3.980	−45.1	8.608	−125.7	2.654	118.2	9.288	101.6
4.097	−48.8	8.923	−129.9	2.985	116.6	9.619	101.1
4.229	−52.8	9.221	−134.2	3.317	115.0	9.951	100.6
4.362	−56.5	9.520	−138.5	3.649	113.8	10.283	100.1
4.511	−60.5	9.802	−142.9	3.980	112.6	10.614	99.6
4.677	−64.6	10.067	−147.2	4.312	111.6	10.946	99.0
4.843	−68.4	10.299	−151.3	4.644	110.7	11.278	98.7
5.042	−72.6	10.532	−155.7	4.976	109.8	11.610	98.1
5.241	−76.5	10.913	−163.9	5.307	109.0	11.941	97.7
5.473	−80.8	11.245	−172.5	5.639	108.3	12.273	97.2
5.705	−84.9	11.500	−180.9	5.971	107.5	12.605	96.8
5.937	−88.7	11.792	−193.8	6.302	106.9	12.936	96.3
6.203	−92.8	12.041	−211.2	6.634	106.1	13.268	95.8

experimental results are collected in Tables 3 and 4. The following values were obtained from the calculations:

$$\beta_1 = (4.2 \pm 0.1) \times 10^5 \ M^{-1}; \qquad \beta_2 = (6.9 \pm 0.5) \times 10^{10} \ M^{-2}$$
$$\beta_3 = (5.3 \pm 0.3) \times 10^{15} \ M^{-3}; \qquad \beta_4 = (1.6 \pm 0.4) \times 10^{19} \ M^{-4}$$

The complex formation curve is drawn in Fig. 1.

DISCUSSION

The potentiometric measurements on the zinc cyanide and the cadmium cyanide systems can be explained by assuming that four mononuclear complexes are formed in both systems. The measurements on the *zinc cyanide* system were rendered difficult by the low solubility of zinc cyanide. The

Table 4. Corresponding values of added volume, v, of titrant and measured emf, E_H, for the cadmium cyanide system (v in ml, and E_H in mV).

Series 7

$E_H^0 = -511.3$ mV
$C_{MS} = 1.000$ mM; $C_{MT} = 1.000$ mM
$C_{AS} = 25.00$ mM; $C_{AT} = 0$ mM
$C_{HS} = 0.00$ mM; $C_{HT} = 50.15$ mM

v	$-E_H$	v	$-E_H$
8.624	−0.3	10.979	136.7
8.956	8.4	11.112	142.6
9.122	13.8	11.278	149.9
9.288	19.7	11.444	157.0
9.453	26.8	11.610	164.5
9.619	35.1	11.775	172.7
9.785	44.9	11.941	182.0
9.851	49.7	12.107	193.7
9.918	54.6	12.273	209.9
9.984	60.1	12.439	241.0
10.051	65.9	12.605	283.0
10.117	72.4		
10.183	79.3		
10.283	89.6		
10.382	99.0		
10.482	107.5		
10.581	114.7		
10.681	121.0		
10.780	126.6		
10.880	131.9		

Series 8

$E_H^0 = -514.3$ mV
$C_{MS} = 2.000$ mM; $C_{MT} = 2.000$ mM
$C_{AS} = 10.07$ mM; $C_{AT} = 0$ mM
$C_{HS} = 0.23$ mM; $C_{HT} = 20.29$ mM

v	$-E_H$	v	$-E_H$
1.493	−31.5	6.833	118.4
1.824	−21.0	7.098	122.4
2.156	−10.1	7.364	125.6
2.620	6.3	7.629	129.6
2.902	16.7	7.911	132.9
3.218	30.0	8.193	137.0
3.483	41.0	8.492	140.6
3.781	53.4	8.790	145.1
3.980	60.7	9.089	148.8
4.213	68.3	9.371	152.7
4.478	75.9	9.653	157.1
4.810	84.1	9.885	161.3
4.976	87.3	10.117	164.7
5.175	91.9	10.349	169.4
5.374	95.3	10.747	177.6
5.573	99.4	11.112	186.6
5.805	102.9	11.361	194.2
6.054	107.3	11.576	202.3
6.302	110.8	11.792	211.9
6.568	115.1	12.008	227.5

Series 9

$E_H^0 = -512.9$ mV
$C_{MS} = 5.00$ mM; $C_{AS} = 25.20$ mM; $C_{HS} = 0.57$ mM
$C_{MT} = 5.00$ mM; $C_{AT} = 0$ mM; $C_{HT} = 50.72$ mM

v	$-E_H$	v	$-E_H$	v	$-E_H$	v	$-E_H$
2.023	−5.0	3.715	69.5	6.103	123.3	8.923	168.9
2.222	3.3	3.881	76.3	6.369	133.3	9.205	172.9
2.388	10.1	4.047	82.5	6.634	137.3	9.487	177.2
2.554	17.2	4.279	90.3	6.899	141.2	10.001	185.6
2.720	24.2	4.578	98.9	7.165	144.9	10.432	193.5
2.886	31.5	4.859	105.9	7.447	148.7	10.797	201.5
3.052	39.0	5.208	113.3	7.745	152.7	11.095	209.1
3.218	46.7	5.407	117.2	8.044	156.8	11.444	220.6
3.383	54.5	5.622	121.2	8.342	160.8	11.891	244.6
3.549	62.2	5.855	125.2	8.641	164.9	12.024	256.6

investigations indicate that a species [$ZnCN^+$] exists, in contrast to the reports of Izatt *et al.*[2] The fact that these authors have not detected the first complex,

may be explained by its rather narrow range of existence. Titrations of alkaline zinc cyanide solutions with perchloric acid result in an increased uncertainty in $\bar{n}$ at the end of the titrations, where the first complex should be determined.

In keeping C_M, C_A, and C_H of about the same magnitude and with the use of a very accurate burette, this uncertainty has been decreased in the present investigations. In addition, the combined amalgam- and pH-measurements give about the same value of β_1 as do the pH-measurements. In view of the large difference in ionic strength, the values of β_2, β_3, and β_4 obtained in the present work in 3 M $NaClO_4$ agree surprisingly well with those reported by Izatt *et al.* at zero ionic strength. The measurements on the *cadmium cyanide* system were not hampered by any precipitation, and a wider range of metal ion concentration could be used. The magnitudes of the stability constants in this investigation, especially of β_1 and β_2, are about the same as those determined by Leden [8] with the use of amalgam electrodes.

In previous investigations of the thiosulfate and acetate systems of zinc and cadmium,[4,5] the cadmium complexes have been found to be considerably stronger than the zinc complexes. For the cyanide systems, this trend is valid only for the first complex, but is reversed for the following ones.

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