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Polarographic Investigation of Dilute Solutions of Cadmium Cyanide Complexes

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A polarographic study of very dilute solutions of zinc perchlorate in the presence of increasing amounts of potassium cyanide has previously been made by the authors[1]. We found that, although the ion $Zn(CN)_4^{--}$ evidently predominates, quite a series of complex zinc cyanide ions are formed, from $Zn(CN)_3^-$ ions to $Zn(CN)_6^{----}$ ions. For the latter Pines[2] in his polarographic studies got no reduction; but we found that it was polarographically reduced before the reduction potential of K^+ is reached, whereas Pines assumes that it does not decompose at lower potentials than -2 volts.

Pines[3] further assumes, in opposition to the results of v. Euler[4], and of later investigators, that the complex ion $Cd(CN)_3^-$ and not the ion $Cd(CN)_4^{--}$ is predominant in dilute solutions of cadmium cyanide complexes.

The question, whether the cyanide complexes of zinc or those of cadmium have the greater instability constant, has also been a matter of investigation and discussion. It has been found that they are of the same order of magnitude[4,5]. If, however, as supposed by Pines[2], the $Zn(CN)_4^{--}$ ion predominates in dilute potassium zinc cyanide solutions, and the $Cd(CN)_3^-$ ion in potassium cadmium cyanide solutions, the constants found are not directly comparable. It seems therefore that a further investigation as regards these phenomena is indicated.

Considering the above mentioned inconsistencies we found it of interest to make a polarographic study of cadmium perchlorate in the presence of increasing amounts of potassium cyanide under practically the same experimental conditions as formerly used for the zinc perchlorate — potassium cyanide solutions.

EXPERIMENTAL PROCEDURE

A polarograph from Radiometer with a photoelectric amplifier, an automatic registrator and a counter current arrangement was used as previously.

We took good precautions against oxygen waves. Hydrogen and nitrogen purified over red hot copper and bubbled through chromous chloride solutions were used. In order to avoid intrusion of air during the passage plastic tubing was substituted for rubber tubing. The solutions in the electrolytic vessel were the whole time kept under one of the above mentioned gasses.

Cadmium perchlorate solutions were prepared by precipitation of cadmium sulphate solutions with equivalent amounts of barium perchlorate solutions.

The molar concentration of the cadmium ions was of the order of magnitude of 10^{-3}. The concentration of potassium cyanide was increased from mole ratio $Cd^{++} : CN^{-} = 1 : 0$ to mole ratio $Cd^{++} : CN^{-} = 1 : 320$.

Inasmuch as some mercurous cyanide undoubtedly is formed during the electrolysis, the stationary pool of mercury on the bottom of the electrolytic cell will give a mixed potential. We therefore found it convenient as a check on our measurements to take a series of readings with a large saturated calomel half-cell as a non-polarizable reference electrode.

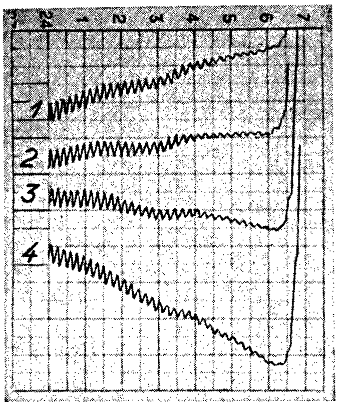

Fig. 1. Electro-reduction of cadmium perchlorate in aqueous solutions.

No	Volts		Counter current	1/sens.	Mol. conc.	
	E.M.F. applied	Starting point			$NaClO_4$	$Cd(ClO_4)_2$
1	2	0	2	1 × 1	0.1	0.0003
2	2	0	3	1 × 1	0.1	0.0003
3	2	0	4	1 × 1	0.1	0.0003
4	2	0	5	1 × 1	0.1	0.0003

EXPERIMENTAL RESULTS

During a previous investigation [6] we found that the polarographic reduction of Cd^{++} ions under certain circumstances can occur successively, the discharge wave being preceded by a smaller one. This pre-wave has been found also by reduction of some other metal ions under similar conditions. At that time an apparatus with counter current was not available, but with our present equipment we make use of a counter current, thereby getting more distinct waves. As will be seen from Fig. 1, which gives the results in pure cadmium perchlorate solutions, the value of the half wave potential for the pre-wave is found to be −0.35 volts against the mercury anode. The increase in current induced by the cadmium starts about −0.65 volts. On addition of cyanide the pre-wave disappears, inasmuch as the half-wave potential for the cadmium ion shifts towards less negative values.

The said value for the half-wave potential, $E_{\frac{1}{2}}$, is the same as formerly found. This is consistent with the assumption that in the presence of a relatively large excess of a stated supporting electrolyte the half-wave potential is fixed as long as the ionic strength is kept constant.

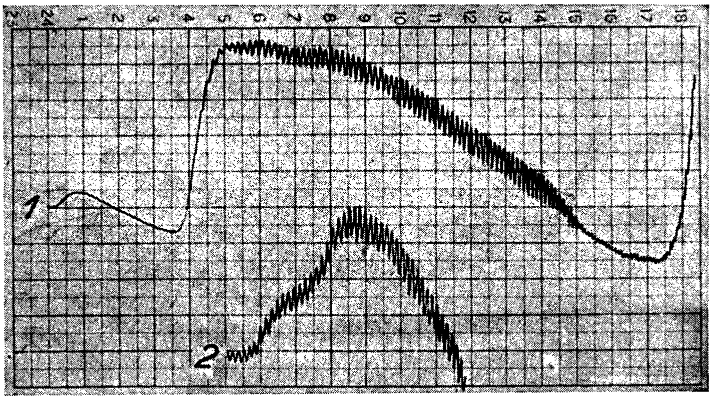

Fig. 2. Electro-reduction of solutions of cadmium perchlorate and potassium cyanide with the molar proportion Cd : CN = 1 : ½.

No	Volts		Counter current	1/sens.	Mol. conc.		
	E.M.F. applied	Starting point			$NaClO_4$	$Cd(ClO_4)_2$	KCN
1	2	0	1	3 × 10	0.1	0.001	0.0005
2	2	−0.5	4	5 × 1	0.1	0.001	0.0005

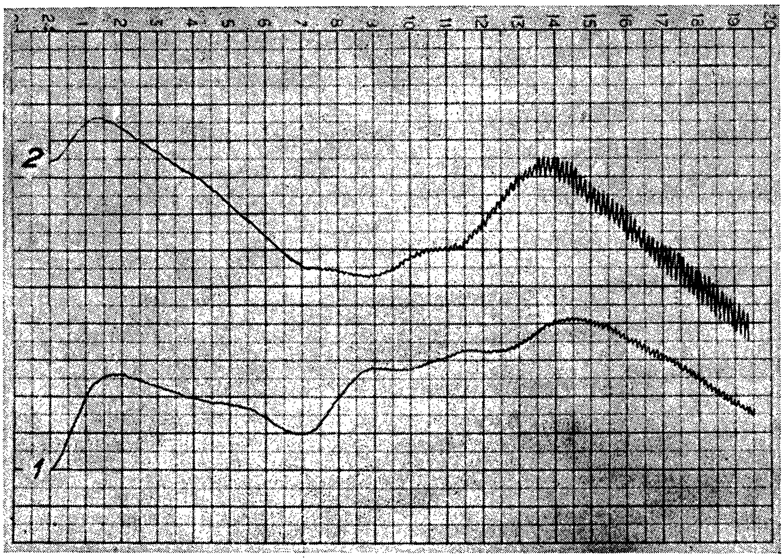

Fig. 3. Electro-reduction of solutions of cadmium perchlorate and potassium cyanide with the molar proportions Cd : CN = 1 : 2 and 1 : 4.

No	Volts		Counter current	1/sens.	Mol. conc.		
	E.M.F. applied	Starting point			$NaClO_4$	$Cd(ClO_4)_2$	KCN
1	1	0	4	1.5 × 10	0.1	0.001	0.002
2	1	0	5	1.5 × 10	0.1	0.001	0.004

On the addition of cyanide we found a shift towards less negative values for the Cd^{++} ion, although an increase of concentration usually entails a shift towards more negative values. The same has been found earlier for zinc.

As the concentration of cyanide increases, the Cd^{++} wave decreases, and when the mole ratio $Cd^{++} : CN^- = 1 : 5$ is reached the wave for the free metallic ion has grown rather ambiguous. At the ratio 1 : 6 it is no more distinguishable.

Simultaneously with the decrease of the discharge wave of the simple ion two continuously increasing complex waves appear. When a molar ratio $Cd^{++} : CN^- = 1 : 6$ has been reached the first complex wave disappears and a third complex wave becomes visible. In its turn the second wave decreases as the third wave increases. At a molar ratio $Cd^{++} : CN^- = 1 : 80$ the second and third waves can be said to be connected. At higher concentrations of cyanide the third complex wave only is present and is gradually reaching a constant height.

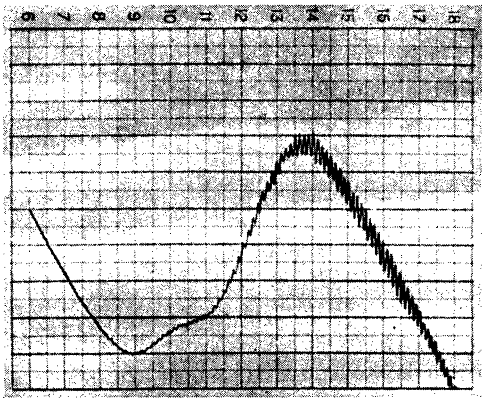

Fig. 4. Electro-reduction of solution of cadmium perchlorate and potassium cyanide with the molar proportion Cd : CN = 1 : 5.

Volts		Counter current	1/sens.	Mol. conc.		
E.M.F. applied	Starting point			$NaClO_4$	$Cd(ClO_4)_2$	KCN
1	−0.3	10	1 × 10	0.1	0.001	0.005

The general trend is the same whether we use a stationary mercury anode or a saturated calomel electrode as anode. With the latter anode we get the usual shift of the half wave potentials to an increased negative value of about 0.25 volts.

Fig. 2 shows that complex formation takes place even before the cyanide has reached the same molar concentration as the cadmium.

The curve taken with the greater sensitivity (2) shows two distinct waves at about −0.6 and −0.8 volts, suggesting that two different complexes have already been formed.

When the concentration of cyanide has grown to be equivalent to that of cadmium, the heights of the complex waves turn out to be of the same order of magnitude as that of cadmium. When the proportion 1 : 4 has been reached the cadmium wave has practically disappeared in relation to the complex waves (Fig. 3).

Even the relatively small increase from the proportion 1 : 4 to the proportion 1 : 5 gives an alteration of the shape of the curve, the cadmium wave having disappeared completely, the first complex wave having become very small in relation to the second wave, which has increased perceptibly. No third complex wave has as yet turned up (Fig. 4).

Even at the relatively small increase of cyanide given by the proportion 1 : 8 the first complex wave has completely disappeared, and the second complex wave has reached its maximal height. At the same time a third complex wave appears. This wave increases very slowly with increasing concentration of cyanide, although the second complex wave

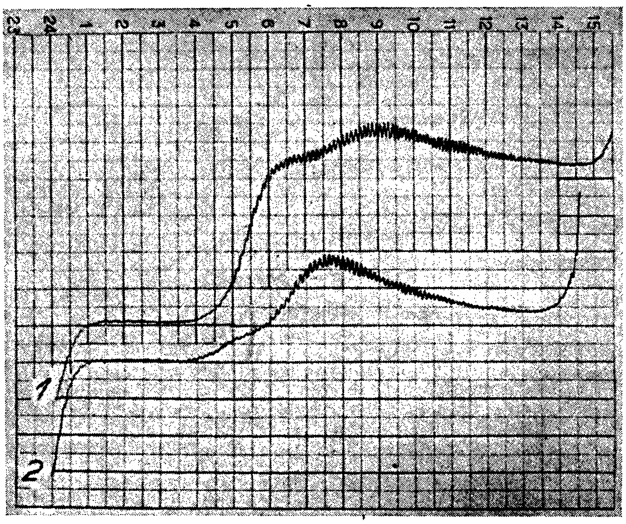

Fig. 5. Electro-reduction of solutions of cadmium perchlorate and potassium cyanide with the molar proportions 1 : 8 and 1 : 40.

No	Volts		Counter current	1/sens.	Mol. conc		
	E.M.F. applied	Starting point			$NaClO_4$	$Cd(ClO_4)_2$	KCN
1	2	0	0	3 × 10	0.1	0.001	0.008
2	2	0	0	3 × 10	0.1	0.001	0.040

Table 1. Height of Waves. Saturated calomel half cell as anode.

$[Cd^{++}]$ / $[CN^-]$	C_1			C_2			C_3		
	H_{obs}	F	H_{calc}	H_{obs}	F	H_{calc}	H_{obs}	F	H_{calc}
1 : 2	10	3 × 10	30	8	3 × 10	24			
1 : 5	—	—	—	23	7 × 10	161	Not measurable		
1 : 8	—	—	—	80	1.5 × 10	120	11	1.5 × 10	17
1 : 14	—	—	—	40	2 × 10	80	22	1.5 × 10	33
1 : 20	—	—	—	7	7 × 10	49	37	1.5 × 10	55
1 : 40	—	—	—	10	1.5 × 10	15	39	1.5 × 10	59
1 : 80	—	—	—	—	—	—	The waves are connected		
1 : 160	—	—	—	—	—	—	80	7 × 1	56
1 : 320	—	—	—	—	—	—	80	7 × 1	56

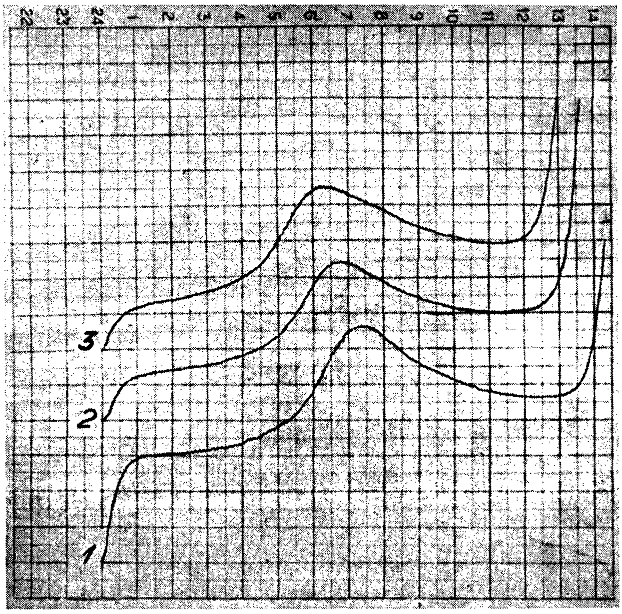

Fig. 6. Electro-reduction of solutions of cadmium perchlorate and potassium cyanide with the molar proportions 1 : 80, 1 : 160 and 1 : 320.

No	Volts		Counter current	1/sens.	Mol. conc.		
	E.M.F. applied	Starting point			$NaClO_4$	$Cd(ClO_4)_2$	KCN
1	2	0	0	3 × 10	0.1	0.001	0.08
2	2	0	0	3 × 10	0.1	0.001	0.16
3	2	0	0	3 × 10	0.1	0.001	0.32

decreases rapidly. When we have reached the proportion 1 : 40 the second complex wave has almost disappeared while the third complex wave is very pronounced (Fig. 5).

At the proportion 1 : 80 the second and the third complex waves are linked together and can not be distinguished from each other. With a very large excess of cyanide one well defined wave only is obtained. This must be ascribed to the third cyanide complex. At the ratios 1 : 160 and 1 : 320 we thus find practically the same curves (Fig. 6).

The figures 7 and 8 give some of the curves resulting from the use of a saturated calomel electrode as anode. The agreement between the two series of curves is good, inasmuch as we find corresponding waves. The form of the curves, however, differ somewhat as we have not used the counter current for the last series.

Fig. 7. Electro-reduction of solutions of cadmium perchlorate and potassium cyanide with the molar proportions 1 : 2, 1 : 8 and 1 : 40. Saturated calomel electrode as anode.

No	Volts		Counter current	1/sens.	Mol. conc.		
	E.M.F. applied	Starting point			$NaClO_4$	$Cd(ClO_4)_2$	KCN
1	2	0	0	3 × 10	0.1	0.001	0.002
2	2	0	0	7 × 10	0.1	0.001	0.008
3	2	−0.6	0	1.5 × 10	0.1	0.001	0.040

DISCUSSION

It might be of interest to give a survey of the change of height of the different complex waves in relation to the increasing concentration of cyanide.

A diagram of the results when a mercury anode is used will be found in Fig. 9. The heights of the different curves are given as ordinates and the relationship $CN^- : Cd^{+\ +}$ as abscissae. The corresponding data with a saturated calomel half cell as anode are given in Table 1 p. 1539.

The graphs show plainly that the cadmium wave decreases very rapidly as the complex waves appear. The first complex wave apparently disappears

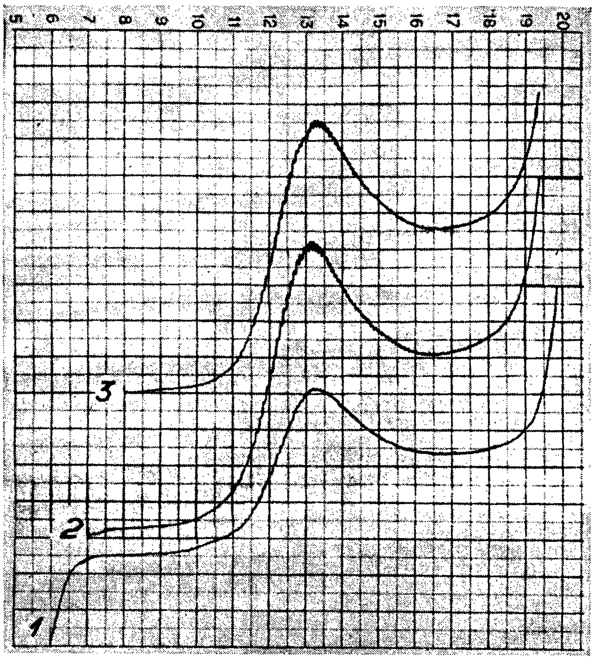

Fig. 8. Electro-reduction of solutions of cadmium perchlorate and potassium cyanide with the molar proportions 1 : 80, 1 : 160 and 1 : 320. Saturated calomel electrode as anode.

No	Volts		Counter current	1/sens.	Mol. conc.		
	E.M.F. applied	Starting point			$NaClO_4$	$Cd(ClO_4)_2$	KCN
1	2	−0.6	0	1.5 × 10	0.1	0.001	0.08
2	2	−0.7	0	7 × 1	0.1	0.001	0.16
3	2	−0.8	0	7 × 1	0.1	0.001	0.32

very abruptly, but the shapes of the polarographic curves suggest that the first and the second complex waves draw together in such a way that they are not to be distinguished from each other. That is also in keeping with the very rapid increase in height of the second complex wave, which reaches a maximum and diminishes rapidly as a third complex wave asserts itself.

It is evident from the diagram that as long as the excess of potassium cyanide does not exceed $Cd^{++} : CN^- = 1 : 20$ the complex corresponding to C_1

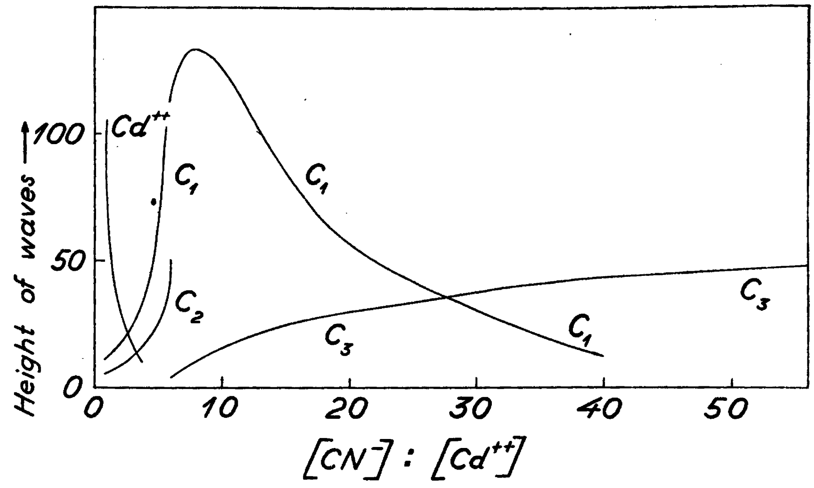

Fig. 9. Diagram of heights of cadmium waves and of cadmium complex waves in relationshipto the proportion $[CN^-]/[Cd^{++}]$.

is predominant. As the excess of cyanide surpasses $Cd^{++} : CN^- = 1 : 30$ the complex corresponding to C_3 prevails. It seems as if those two complexes may lay claim to special interest. The highest complex (curve C_3) appears when the excess of CN^- over Cd^{++} passes 6 : 1. When the excess grows very great, no increase in the height of the wave is observed and the C_1 curves disappear at $Cd^{++} : CN > 1 : 40$. It therefore seems reasonable to ascribe the C_3 curve to the complex ion $Cd(CN)_6^{----}$, which is the highest described cadmium cyanide complex ion.

The curve marked C_2 must indicate a lower cyanide complex than $Cd(CN)_6^{----}$. According to earlier research workers such as Britton and Dodd [5], who measured changes in pH with increase of cyanide, and Glasstone [7], who made an electrode potential titration curve for cadmium sulphate with sodium cyanide and a cadmium electrode, the $Cd(CN)_4^{--}$ ions are chiefly present in solution. Glasstone maintains that a $Cd(CN)_3^-$ ion is also indicated, whilst Britton and Dodd confine themselves to asserting that an anion having a lower cyanide content than that corresponding to $Cd(CN)_4^{--}$ must exist in solution.

Our curves then seem to show that beside the $Cd(CN)_4^{--}$ ion, which is predominant between the above mentioned concentrations (C_1), a lower complex ion, which we assume to be $Cd(CN)_3^-$, (C_2) exists in solutions having an excess of cyanide less than $Cd^{++} : CN = 1 : 6$. On further increase of cyanide this ion is not polarographically traceable.

SUMMARY

1. The polarographic behaviour of the system $Cd(ClO_4)_2$-KCN-H_2O has been investigated.

2. Even at quite small additions of cyanide ions complex waves appear, showing that cadmium cyanide complexes have been formed.

3. At an excess of cyanide greater than $Cd^{++} : CN = 1 : 4$ the cadmium wave has disappeared, and the complex waves dominate.

4. At the interval between $Cd^{++} : CN = 1 : 4$ and $Cd^{++} : CN = 1 : 20$ the complex ion $Cd(CN)_4^{--}$ dominates.

5. At a greater excess than $Cd^{++} : CN^- = 1 : 30$ the complex ion $Cd(CN)_6^{----}$ prevails. When the proportion $Cd^{++} : CN^-$ grows greater than $1 : 40$ no other cadmium cyanide complex can be polarographically detected.

6. In solutions with a relatively small cyanide content still another complex is evident. We suggest that ion to be $Cd(CN)_3^-$.

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