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METAL AMMINE FORMATION IN AQUEOUS SOLUTION V

STABILITY OF THE ZINC AND CADMIUM ETHYLENEDIAMINE IONS AND THE CO-ORDINATION NUMBERS OF THE METAL IONS

BY

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I. Introduction[1] and Theoretical Part.

WERNER and SPRUCK[2] have prepared a series of tri-ethylenediamine zinc and cadmium salts which, according to cryoscopic measurements, only to a slight degree split off ethylenediamine in aqueous solution. Thus they possess rather high stability and can stand recrystallization from water. Ethylenediamine has the co-ordination capacity 2, and the 3 ethylenediamine molecules must therefore be assumed to occupy 6 co-ordination positions in all, as in other salts of this type. J. BJERRUM[3] has previously, by means of hydrogen electrode measurements, determined the complexity constants for the formation of the tri-ethylenediamine complexes of some of the divalent metal ions of the iron group, and found that the manganous, the cobaltous, the ferrous and the nickel ions with about equal strength bind all 3 ethylenediamine molecules taken up (see Table 1). Using the terminology of J. BJERRUM[4] this may be expressed by saying that the characteristic and the maximal co-ordination number is the same, namely 6. The characteristic co-ordination number is defined as the number of the first firmly and uniformly bound ligand groups. In many instances it is smaller than the maximal co-ordination number which denotes the maximal number of ligand groups bound in the co-ordinatively saturated complex. In their behaviour towards

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[1] The earlier papers in this series are: J. BJERRUM: Untersuchungen über Kupferammoniakverbindungen I, II, III, D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd., XI, No. 5 (1931), XI, No. 10 (1932), XII, No. 15 (1934), and J. BJERRUM: Metal Ammine Formation in Aqueous Solution — Theory of the Reversible Step Reactions, Doctoral thesis, Copenhagen 1941. These papers are in the following referred to as I, II, III, and IV, respectively.

[2] Zeitschr. anorg. Chem. **21** (1899) 221.

[3] IV, pp. 198 ff.

[4] IV, pp. 80 ff.

Table 1. Consecutive formation constants found for a series of metal ethylenediamine systems.

The values in parenthesis are statistically corrected.

Me	log k_1	log k_2	log k_3	t°	Medium
Zn^{++}	5.92	5.15 (6.23)	1.86	25°	1 N KNO_3
Cd^{++}	5.63	4.59 (5.67)	2.07	»	»
Mn^{++}	2.73	2.06 (2.74)	0.88 (2.53)	30°	1 N KCl
Fe^{++}	4.28	3.25 (3.93)	1.99 (3.64)	»	»
Co^{++}	5.89	4.83 (5.51)	3.10 (4.75)	»	»
Ni^{++}	7.66	6.40 (7.08)	4.55 (6.20)	»	»

ammonia and many other ligands, the zinc and cadmium ions have the characteristic co-ordination number 4[1] (see Table 2). It might therefore be expected that they had the same co-ordination number in the ethylenediamine systems, and that the 3rd ethylenediamine molecule would be more loosely bound than the first two taken up. The formation constants determined for the zinc and cadmium tri-ethylenediamine complexes (recorded in Table 1) show that this is actually so. It will be seen that the effect is not particularly great, but, as in the corresponding ammonia systems, the zinc system more markedly than the cadmium system has the characteristic co-ordination number 4. The first 2 constants lie closer to each other, and the distance to the 3rd constant is greater than in the cadmium system. The values for log k_2 given in parenthesis are statistically corrected in accordance with the characteristic co-ordination number 4, and on the assumption that the di-ethylenediamine complexes have tetrahedral configuration.[2] On the assumption stated, the 2nd ethylenediamine molecule may be taken up in 6 ways, and split off in 2 ways, from which it follows that log k_1 for statistical reasons must be log 12 = 1.08 higher than log k_2. It is seen that the statistical correction just about explains the difference between the values found for log k_1 and log k_2. With regard to the great difference between the 2nd and the 3rd constant it is reasonable to assume a rearrangement from tetrahedral to octahedral configuration at the uptake of the 3rd ethylenediamine molecule.

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[1] Cf. IV, pp. 65 and 152 ff.

[2] From what is known regarding the stereochemical properties of the metal ions, the zinc and cadmium ions never show planar, but always either tetrahedral or octahedral configuration (cf. IV, p. 102).

Table 2. Consecutive formation constants for some metal ammonia systems in 2 N ammonium nitrate at 30°.

The values in parenthesis are statistically corrected.*

Me	$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	$\log k_5$	$\log k_6$	$\frac{d \log k_n}{d t°}$	$\frac{d \log k_n}{d C_{NH_4^+}}$
Zn^{++}	2.37	2.44	2.50	2.15	—	—	−0.008	0.095
		(2.87)	(3.28)	(3.36)				
Cd^{++}	2.65	2.10	1.44	0.93	−0.4	−1.7	−0.008	0.070
		(2.53)	(2.22)	(2.14)				
Co^{++}	2.11	1.63	1.05	0.76	0.18	−0.62	−0.005	0.062
		(2.01)	(1.70)	(1.66)	(1.36)	(0.94)		
Ni^{++}	2.795	2.24	1.73	1.19	0.75	0.03	−0.007	0.061
		(2.62)	(2.38)	(2.09)	(1.93)	(1.59)		

* See IV, pp. 39 ff. and 54 ff.

For comparison, Table 1 records the previously found consecutive formation constants for the ethylenediamine systems of the divalent metal ions of the iron group. In these systems $\log k_2$ and $\log k_3$ are corrected for the statistical effect assuming octahedral configuration and that the 2nd ethylenediamine molecule may equally well be bound in planar and in angular position relative to the first one taken up, but that in the former case there is steric hindrance for the uptake of the 3rd ethylenediamine molecule[1].

The experimentally determined constants permit us to compute the distribution of the metal ions on the particular complexes at different concentrations of ethylenediamine. Fig. 1 is a graphical representation of the ranges of existence of the different complex ions. The diagram plainly shows that the zinc and cadmium di-ethylenediamine complexes have a range of existence substantially wider than that of the other complex ions.

The available data on the complexity constants make it possible to say something regarding the extent to which the "bridge" between the 2 amino groups in ethylenediamine strengthens the bond between the amine group and the metal ions. The logarithm of the consecutive constants furnishes a direct measure

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[1] For further details, see IV, p. 94.

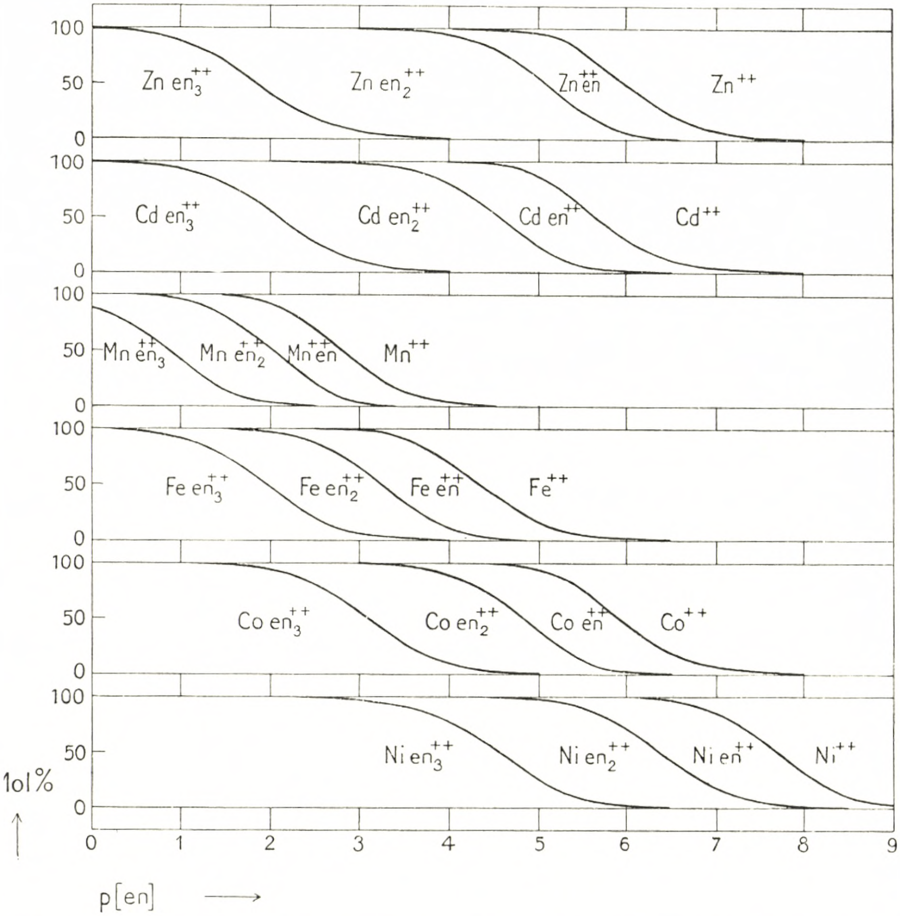

Fig. 1. Distribution of the metal ions on the different complex ions in a series of metal ethylenediamine systems. For the zinc and the cadmium systems in 1 N KNO_3 at 25°, and for the divalent metal ions of the iron group in 1 N KCl at 30°.

of the affinity between the metal ion and the amine molecule. The affinity, or the maximum work, at the binding of the n'th amine molecule in a 1 molar amine solution is thus given by he expression

$$A = RT \ln k_n . \tag{1}$$

f we denote the product of constants $k_1 k_2 \cdots k_N$ by K_N, the following expression applies analogously to the mean affinity at the binding of the N first amine molecules

$$A_{Mean} = \frac{1}{N} RT \ln K_N . \tag{2}$$

Table 3. Comparison of the mean affinity (in kg. cal.) for the binding of one ethylenediamine and two ammonia molecules in some metal amine systems.

	$\frac{1}{2}$ RT ln K_4 (NH_3)	$\frac{1}{2}$ RT ln K_2 (en)
Zn^{++} . . .	6.45	7.54
Cd^{++} . . .	4.85	6.96
	$\frac{1}{3}$ RT ln K_6 (NH_3)	$\frac{1}{3}$ RT ln K_3 (en)
Co^{++} . . .	2.36	6.38
Ni^{++} . . .	4.03	8.59

Table 3, for the zinc, cadmium, cobaltous, and nickel ion, shows the values of the mean affinity at the binding of one ethylenediamine molecule and two ammonia molecules, calculated by means of (2), when N is put equal to the characteristic co-ordination number in the ammonia systems, and to one-half of the characteristic co-ordination number in the ethylenediamine systems. It is seen that the cobaltous and nickel ions bind one ethylenediamine molecule with a far greater affinity than two ammonia molecules, but that the difference in the case of the cadmium ion and especially the zinc ion is far smaller. Considering that the aliphatic monamines are bound less firmly than ammonia to the ions in question,[1] it may, however, be concluded that also in the case of the zinc ion there is a considerable "chelate" action. The particularly great "chelate" action in the case of the nickel and the cobaltous ions is perhaps explainable by the circumstance that the configuration is tetrahedral in the zinc and cadmium systems and octahedral in the cobaltous and nickel systems.[2] It is not a simple question of the size of the ions, as the cobaltous and nickel ions have ionic radii which lie between those of the zinc and cadmium ions.[3]

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[1] A. Tamisier, Bull. Soc. Chim. [4] **53** (1933) 97, 157.

[2] According to Pauling's theory, d-eigenfunctions are necessary for the establishment of strong octahedral bonds. In this connection it is of interest that the characteristic co-ordination number 6 (at least in so far as the mono- and divalent metal ions are concerned) has been found only in the case of metal ions with unsaturated d-shells.

[3] See IV, p. 74.

II. Experimental Part.

1. Procedure in computing the formation curve for the metal ethylenediamine systems.

As in the earlier investigations of the ethylenediamine systems of the metal ions of the iron group, the formation curve —*i. e.* the relation between the average number of ethylenediamine molecules bound per metal atom ($\bar{n}$), and the negative logarithm of the concentration of free ethylenediamine (p[en]) —is established by determination of the hydrogen ion concentration and used in calculating the constants of the system. The measurements were carried out in solutions with known contents of nitric acid, zinc, or cadmium nitrate and ethylenediamine. Moreover, all solutions were made 1 N with respect to potassium nitrate, in order to establish conditions under which it was possible, with approximation, to apply the classic law of mass action.

Ethylenediamine is able to take up 2 hydrogen ions; this somewhat complicates the computation of the formation curve on the basis of hydrogen ion measurements. Following the usual practice of complex chemistry we shall denote ethylenediamine by en and its 2 acid forms by enH^+ and enH_2^{++}. The 2 consecutive acid dissociation constants of the diammonium ion will be denoted by $k_{enH_2^{++}}$ and k_{enH^+}, respectively. Concentrations of single ions or molecules are designated by the symbol being put in square brackets. In the solution we know:

C_{HNO_3} total nitric acid concentration
C_{Me} total concentration of the complex-forming metal ion
C_{en} total ethylenediamine concentration,

and determine the hydrogen ion concentration $[H^+]$.

For the computation of the formation curve we shall furthermore introduce the following quantities in the acid-base system of the ethylenediamine:

C'_{en} total concentration of ethylenediamine not complex-bound

$$C'_{en} = [en] + [enH^+] + [enH_2^{++}] \tag{3}$$

C_s total concentration of hydrogen ions bound to ethylenediamine

$$C_s = C_{HNO_3} - [H^+] + [OH^-] = [enH^+] + 2[enH_2^{++}] \tag{4}$$

$$\alpha_{en} = \frac{[en]}{C'_{en}} = \frac{k_{enH_2^{++}} k_{enH^+}}{k_{enH_2^{++}} k_{enH^+} + k_{enH_2^{++}}[H^+] + [H^+]^2} \tag{5}$$

$$\bar{n}_{en} = \frac{C_s}{C'_{en}} = \frac{k_{enH_2^{++}}[H^+] + 2[H^+]^2}{k_{enH_2^{++}} k_{enH^+} + k_{enH_2^{++}}[H^+] + [H^+]^2}. \tag{6}$$

The expression for α_{en} and $\bar{n}_{en}$, *i. e.* the fraction of ethylenediamine in the acid-base system which is present as free ethylenediamine, and the average number of hydrogen ions bound to the ethylenediamine, are derived as usual by introducing mass action expressions for the acid dissociation constants.

The formation function for the complex system, $\bar{n}$, is calculated from the expression

$$C_{en} = [en] + [enH^+] + [enH_2^{++}] + \bar{n} \cdot C_{Me}. \tag{7}$$

Solving (7) with respect to $\bar{n}$ and introducing $\bar{n}_{en}$ and C_s by means of (3) and (6) we find

$$\bar{n} = \frac{C_{en} - \frac{C_s}{\bar{n}_{en}}}{C_{Me}}. \tag{8}$$

Combining (5) and (6) leads to the concentration of free amine

$$[en] = C_s \frac{\alpha_{en}}{\bar{n}_{en}} \tag{9}$$

or for the free ligand exponent

$$p[en] = -\log[en] = \log\frac{\bar{n}_{en}}{\alpha_{en}} - \log C_s. \tag{10}$$

It is seen that $\bar{n}$ and p[en] are readily calculated if we know $\bar{n}_{en}$ and $\frac{\bar{n}_{en}}{\alpha_{en}}$. Moreover, that these quantities may be calculated by means of (5) and (6), provided the acid-base constants of the ethylenediamine are known.

2. Acid-base constants of ethylenediamine at the salt concentrations used.

The majority of the zinc or cadmium ethylenediamine solutions measured had the following total concentrations[1]: $C_{HNO_3} = 0.1$, $C_{Me} = 0.1$, $C_{en} > 0.05$, and $C_{KNO_3} = 1.00$. Consequently nitric acid is bound to ethylenediamine, and it is only the excess of base which to a higher or lower degree is bound to the complex-forming metal ions. In order to carry out an accurate computation of the complex formation on the basis of the hydrogen ion concentration, it is necessary first to determine the acid-base constants of the ethylenediamine in the particular salt medium. These constants were determined by measurements of a series of ethylenediamine solutions having the same concentration of nitric acid and potassium nitrate as the complex solutions, but having the concentration of complex-forming metal ions replaced by an equivalent amount of barium salt. It is hardly to be assumed that the barium ion may bind ethylenediamine at the small concentrations of amine with which we are concerned here. A few measurements were also made of solutions with $C_{HNO_3} = 0.1$ and $C_{KNO_3} = 1.1$, completely without any addition of salt of the type MeX_2.

The hydrogen ion concentration was determined by means of the glass electrode, by measuring the solution against standard acid solutions having analogous salt concentrations. Thus in the main experiments the standard acid solution had the composition $C_{HNO_3} = 0.005$, $C_{BaCl_2} = 0.1$, $C_{KNO_3} = 1.1$, and in the measurements of the solutions to which no salt of the type MeX_2 had been added, the composition was $C_{HNO_3} = 0.005$, $C_{KNO_3} = 1.2$. In the standard solutions the hydrogen ion concentration is chosen so small that we may reckon that the diffusion potential (against saturated potassium chloride) is the same as for the ethylenediamine solutions. The hydrogen ion concentration $[H^+]$ and the hydrogen ion exponent pH may therefore (at 25°) be calculated directly from the expression

$$pH = -\log [H^+] = \frac{E_{(st.)} - E}{0.591} + pH_{(st.)}, \qquad (11)$$

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[1] All concentrations, here and in what follows, are given in moles per liter of solution.

where the quantities with the subscript (st.) refer to the standard solution.

a. Experimental.

For the glass electrode measurements we used a "Radiometer" valve potentiometer, Model PHM3, with the usual standard equipment: Glass bulb electrode with built-in silver-silver chloride electrode, and as reference electrode a saturated calomel electrode in liquid connection with the measuring vessel. The glass electrode was especially selected and proved to have theoretical pH-dependence even in rather strongly alkaline ethylenediamine solutions with pH close to 10. The glass electrode potential adjusted itself in the course of a couple of minutes, and the liquid in the measuring vessel, about 8 ml, was exchanged a couple of times before the final readings were made. Upon repetition, the potential could be reproduced with an uncertainty of about 0.3 millivolt. The whole glass electrode set-up was placed in an electrically heated air thermostat with strong circulation, so that is was possible to keep the temperature at $25° \pm 0.2°$.

As control, the glass electrode was supplemented by a hydrogen-gas electrode in the most alkaline solutions. The hydrogen electrode functioned excellently in the alkaline nitrate solutions,[1] but of course it was not possible to use it in the standard acid solutions containing nitric acid. Instead, the alkaline nitrate solution was measured against a standard acetate solution, which in turn was measured against the standard acid solution by means of the glass electrode. The hydrogen electrode measurements were carried out in the usual manner with a platinized platinum electrode in an electrode vessel of the type used by S. P. L. Sørensen. The hydrogen was obtained from a flask, washed in sulphuric acid and sodium hydroxide and further purified by being led over red-hot copper. With the aid of a thermocouple it was found that the temperature in the electric furnace was about 500°. The reference electrode was a 1 N calomel electrode, prepared according to Gjaldbæk,[2] in an electrode vessel of the model introduced by Lewis, Brighton, and

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[1] See IV, p. 208.

[2] D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd., V, No. 9 (1924).

Sebastian,[1] which permits rinsing of the siphon tube. The electrodes were placed in an electrically heated water thermostat and were in liquid connection with each other through a saturated solution of potassium chloride. In all cases the temperature was 25° ± 0.05°. The determination of the potentital was carried out by means of a Wolff potentiometer (15000 ohms resistance, smallest graduation 0.01 millivolt) and an Original Moll Galvanometer (from Kipp & Zonen). A calibrated Weston standard cell was used.

The different solutions were prepared in calibrated measuring flasks, by weighing or pipetting from stock solutions of potassium nitrate, barium chloride, nitric acid, and ethylenediamine. The stock solutions of potassium nitrate (2 molar) and barium chloride (1 molar) were made from Merck's preparations ("zur Analyse"). Solutions of the salts in question, with 0.005 mole of nitric acid added per liter, were measured by means of the glass electrode against analogous solutions with 10 times less nitric acid per liter. In this way we found a minor deviation from Nernst's Law, corresponding to a basic impurity of 0.00004 equivalent per liter in the potassium nitrate solution without barium chloride, and 0.00006 equivalent per liter in the standard solution to which barium chloride had been added. The hydrogen ion concentration of the 0.005 molar standard solutions is therefore about 1 per cent. smaller than that corresponding to the amount of nitric acid added. The correction was made in the case of the standard solutions, but is without any significance as regards the other solutions having a substantially higher total concentration of nitric acid.

The nitric acid solutions were prepared from a boiled 5 molar solution.

The ethylenediamine was a pure commercial product of ethylenediamine hydrate, from Schuchardt. It was distilled in a "Schliff" apparatus, and the fraction 118°—119° (almost the whole portion) was collected. The specific gravity was found to be about 0.965 at 21°. By titration with 1 n hydrochloric acid (methyl orange as indicator) it was found to contain 76.2 per cent. ethylenediamine; for the hydrate the value of 76.94 per cent. was calculated. As stock solution served a solution

[1] Journ. Amer. Chem. Soc., **39** (1917) 2251.

of the hydrate, diluted approximately 4 times, which was kept CO_2-free in a bottle with tightly fitting glass stopper. The solution was adjusted according to weight, and weighed-off portions were added to the various salt solutions.

b. Measurements.

The acid-base constants of the ethylenediamine, determined by means of glass and hydrogen electrode, are recorded in Tables 4 and 5. The accurate composition of the standard solutions was as follows:

	C_{KNO_3}	C_{BaCl_2}	C_{HNO_3}	$pH_{(st.)}$(corr.)
Table 4	1.100	0.100	0.00499	2.307
Table 5	1.200	0	0.00500	2.304

The difference in potential between these standard solutions and the 0.1 N standard acetate solution used in the hydrogen electrode measurements was determined by means of the glass electrode, and found to be on an average 0.1400 and 0.1398 volt at 25°. In the tables, $E_{(st)} - E$ (4th column) shows the potential measured against the standard solutions, and pH (5th column) the hydrogen ion exponent calculated from this value with the aid of (11). In all solutions investigated, the hydrogen ion concentration and the hydroxyl ion concentration are so small that the mean number of hydrogen ions bound per molecule of ethylenediamine ($\bar{n}_{en}$, 3rd column) is given by the expression

$$\bar{n}_{en} = \frac{C_{HNO_3}}{C_{en}}.$$

The connection between $\bar{n}_{en}$, the hydrogen ion concentration, and the acid dissociation constants is expressed in (6). Solving this equation with respect to $k_{enH_2^{++}}$ and k_{enH^+} and transforming the particular expresssions we arrive at

$$pk_{enH_2^{++}} = pH + \log\frac{\bar{n}_{en} - 1}{2 - \bar{n}_{en}} + \log\left(1 + \frac{\bar{n}_{en} \cdot k_{enH^+}}{(\bar{n}_{en} - 1)\,[H^+]}\right) \quad (12)$$

$$pk_{enH^+} = pH + \log\frac{\bar{n}_{en}}{1 - \bar{n}_{en}} - \log\left(1 + \frac{(2 - \bar{n}_{en})\,[H^+]}{(1 - \bar{n}_{en})\,k_{enH_2^{++}}}\right). \quad (13)$$

Table 4. Acid-base constants of ethylenediamine at 25° in 1 N potassium nitrate solution containing barium chloride.

$$C_{KNO_3} = 0.998,\ C_{BaCl_2} = 0.100$$

$$C_{HNO_3} = 0.1003 \text{ (Nos. 9, 10, 12, 13, 16) and } 0.1006 \text{ (All other Nos.)}$$

$$pH_{(st.)} = 2.307.$$

$$\Delta = \frac{\bar{n}_{en} \cdot 10^{-10.17}}{(\bar{n}_{en} - 1)[H^+]}$$

No.	C_{en}	$\bar{n}_{en}$	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en} - 1}{2 - \bar{n}_{en}}$	$\log(1 + \Delta)$	$pk_{enH_2^{++}}$ glass
1.....	0.06326	1.589	0.2969	7.330	+0.156	0.002	7.488*
2.....	0.07028	1.431	0.3131	7.605	−0.120	0.004	7.489
3.....	0.07110	1.415	0.3143	7.625	−0.149	0.004	7.480
4.....	0.07202	1.397	0.3173	7.675	−0.182	0.006	7.490*
5.....	0.07273	1.383	0.3196	7.715	−0.207	0.006	7.514
6.....	0.07600	1.324	0.3243	7.794	−0.319	0.008	7.478*
7.....	0.08203	1.227	0.3371	8.010	−0.532	0.016	7.497*
							7.492

$$\Delta = \frac{(2 - \bar{n}_{en})[H^+]}{(1 - \bar{n}_{en})\,10^{-7.49}}$$

No.	C_{en}	$\bar{n}_{en}$	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{1 - \bar{n}_{en}}$	$\log(1 + \Delta)$	pk_{enH^+} glass	pk_{enH^+} hydr.
8....	0.1043	0.9648	0.3950	8.991	1.438	0.287	(10.142*)	
9....	0.1111	0.9028	0.4116	9.271	0.968	0.074	10.165	
,,....	,,	,,	0.41245	9.285	,,	0.073		10.180
10....	0.1206	0.8317	0.4254	9.505	0.694	0.028	10.171	
,,....	,,	,,	0.42605	9.516	,,	0.027		10.183
11....	0.1229	0.8186	0.4268	9.529	0.654	0.026	10.157*	
12....	0.1373	0.7305	0.4401	9.754	0.433	0.011	10.176	
,,....	,,	,,	0.4409	9.767	,,	,,		10.189
13....	0.1486	0.6750	0.4465	9.862	0.318	0.007	10.173	
,,....	,,	,,	0.4478	9.884	,,	,,		10.195
14....	0.1547	0.6509	0.4491	9.906	0.270	0.006	10.170*	
15....	0.1615	0.6229	0.4523	9.960	0.218	0.005	10.173*	
16....	0.2524	0.3974	0.4773	10,383	−0.181	0.002		10.200

* For the making of these measurements the authors are indebted to Mr. ERLING JUHL NIELSEN.

Expression (12) is valid only for values of $\bar{n}_{en} > 1$, and (13) for $\bar{n}_{en} < 1$. The reciprocal influence of $k_{enH_2^{++}}$ and k_{enH^+} finds its expression in the last term, but is so small that the constants may be calculated from the first two terms alone, provided $\bar{n}_{en} > 1.5$ or < 0.5. This is seen from Tables 4 and 5,

Table 5. Acid-base constants of ethylenediamine at 25° in 1.1 N potassium nitrate without barium chloride.

$$C_{KNO_3} = 1.099$$

$$C_{HNO_3} = 0.0995 \text{ (Nos. 1—2) and } 0.1003 \text{ (Nos. 3—4)}$$

$$pH_{(st.)} = 2.304.$$

$$\Delta = \frac{\bar{n}_{en} \cdot 10^{-10.17}}{(\bar{n}_{en} - 1)[H^+]}$$

No.	C_{en}	$\bar{n}_{en}$	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en} - 1}{2 - \bar{n}_{en}}$	$\log(1 + \Delta)$	$pk_{enH_2^{++}}$ glass
1.....	0.05963	1.669	0.2874	7.167	0.306	0.001	7.474
2.....	0.06559	1.517	0.3042	7.451	0.029	0.003	7.483

$$\Delta = \frac{(2 - \bar{n}_{en})[H^+]}{(1 - \bar{n}_{en})\ 10^{-7.48}}$$

No.	C_{en}	$\bar{n}_{en}$	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{1 - \bar{n}_{en}}$	$\log(1 + \Delta)$	pk_{enH^+} glass	pk_{enH^+} hydr.
3.....	0.1175	0.8536	0.4221	9.446	0.765	0.036	10.175	
„.....	„	„	0.4222	9.448	„	„		10.177
4.....	0.1484	0.6759	0.4480	9.884	0.319	0.007	10.196	
„.....	„	„	0.44765	9.878	„	„		10.190

which, besides the constants found, give the values of the individual terms in the calculation.

The values of pk_{enH^+} determined by means of the hydrogen electrode are on an average a little higher than those found by means of the glass electrode, but the difference is slight, and shows that the glass electrode employed functions excellently in even the most alkaline of the solutions investigated. The variation in the values found for $pk_{enH_2^{++}}$ is purely incidental. pk_{enH^+}, however, seems on the whole to increase a little with rising ethylenediamine concentration. J. BJERRUM[1] has previously determined pk_{enH^+} in 1 N potassium nitrate solution at 30°, using the hydrogen electrode, and found it to be 9.94; at salt concentrations corresponding to those in Table 1 the value is estimated to be 9.98. The value here found at 25° is 10.18. With use of these figures, a calculation is made of the heat of

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[1] IV, p. 208.

neutralization at the uptake of the 1st hydrogen ion by the ethylenediamine, the result being 16.5 kg. cal. This value undoubtedly is too high,[1] but nevertheless of the right order of magnitude, and indicates the mutual agreement between the measurements concerned.

3. Formation curves for the zinc and cadmium ethylenediamine ions.

a. Measurements.

The experimental data for the establishment of the formation curves for the zinc and cadmium ethylenediamine ions are recorded in Tables 6 and 7. The solutions were prepared and the measurements were made as described in the preceding chapter. The approximately 1 molar stock solutions of zinc and cadmium nitrate (Merck, purum) were standardized according to R. Berg[2] by precipitation with 8-hydroxy-quinoline in weak acetic acid solution, with both weighing and bromine titration of the precipitate. pH of the stock solutions was about 4, *i. e.* a value which approximately corresponds to the hydrolysis of the pure salts and proves that the presence of acid and basic impurities in the salts employed may be ignored. The composition of the zinc and cadmium solutions investigated is recorded in the tables. In most of the solutions the concentration of zinc and cadmium nitrate is approximately 0.1 molar, and in the remaining ones 0.05 molar, to the latter solutions, however, an equivalent amount of barium chloride or barium nitrate is added, so that the total concentration of divalent metal ion in all solutions is about 0.1 molar. In some of the solutions with halved heavy metal concentration, the nitric acid concentration is likewise halved and the potassium nitrate concentration increased to 1.05; otherwise the concentrations are the usual, $C_{HNO_3} = 0.100$ and $C_{KNO_3} = 1.00$.

The solutions all proved to be stable and did not show any precipitation upon standing.

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[1] According to M. Berthelot, Ann. chim. phys. [7] **20** (1900) p. 163, the heat of neutralization at the uptake of the first hydrogen ion is 12.4 kg. cal., and for the second hydrogen ion 10.8 kg. cal.

[2] Zeitschr. analyt. Chem. **71** (1927) 174, 321.

Table 6. Glass electrode measurements of ethylenediamine containing zinc salt solutions at 25°.

Calc. with $pk_{enH_2^{++}} = 7.49$, $pk_{enH^+} = 10.17$ ($pH < 9.30$) and $pk_{enH^+} = 10.18$ ($pH > 9.30$). $pH_{(st.)} = 2.307$.

$C_{HNO_3} = 0.1006$, C_{KNO_3} 0.998

No.	C_{Zn}	C_{en}	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{\alpha_{en}}$	$\bar{n}_{en}$	C'_{en}	$\bar{n}$	p[en]
1	0.1001	0.0596	0.2174	5.986	5.996	1.969	0.0511	0.085	6.993
2	0.1226	0.0718	0.2264	6.137	5.697	1.958	0.0514	0.167	6.694
3	0.0993	0.1094	0.2477	6.499	4.985	1.906	0.0528	0.570	5.982
4	0.1220	0.1312	0.2503	6.542	4.901	1.899	0.0530	0.641	5.898
5	0.1000	0.1728	0.2670	6.824	4.358	1.822	0.0552	1.176	5.355
6	0.0992	0.2047	0.2777	7.005	4.017	1.753	0.0574	1.486	5.014
7	0.1218	0.2644	0.2865	7.115	3.814	1.703	0.0591	1.686	4.811
8	0.1002	0.2473	0.2969	7.331	3.428	1.590	0.0633	1.840	4.426
9	0.0997	0.2748	0.3239	7.787	2.686	1.331	0.0756	1.998	3.683
10	0.1002	0.2909	0.3437	8.122	2.214	1.181	0.0852	2.053	3.211
11	0.1000	0.3286	0.3897	8.901	1.302	0.986	0.1020	2.266	2.299
12	0.1219	0.4150	0.4131	9.297	0.886	0.897	0.1122	2.484	1.883
13	0.0995	0.3781	0.4243	9.486	0.703	0.842	0.1195	2.599	1.700
14	0.0995	0.3990	0.4340	9.650	0.530	0.768	0.1310	2.694	1.527
15	0.0993	0.4714	0.4602	10.093	0.080	0.552	0.1823	2.912	1.087

$C_{HNO_3} = 0.0498$, $C_{Ba(NO_3)_2} = 0.050$, $C_{KNO_3} = 1.050$.

No.	C_{Zn}	C_{en}	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{\alpha_{en}}$	$\bar{n}_{en}$	C'_{en}	$\bar{n}$	p[en]
16	0.05005	0.03508	0.2395	6.360	5.257	1.931	0.02576	0.186	6.560
17	0.04970	0.06464	0.2640	6.774	4.453	1.839	0.02706	0.756	5.756

$C_{HNO_3} = 0.1006$, $C_{BaCl_2} = 0.050$, $C_{KNO_3} = 0.998$.

No.	C_{Zn}	C_{en}	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{\alpha_{en}}$	$\bar{n}_{en}$	C'_{en}	$\bar{n}$	p[en]
18	0.05048	0.07516	0.2439	6.434	5.112	1.920	0.05240	0.451	6.109
19	0.04975	0.09730	0.2580	6.672	4.649	1.868	0.05385	0.873	5.646

An attempt was made to measure one of the more alkaline zinc solutions (Nr. 14) by means of the hydrogen electrode. This was considered possible, owing to the place of zinc in the electro-chemical series, but we did not succeed in obtaining definite potentials, perhaps because of the large nitrate content of the solutions. Hence the hydrogen ion concentration was determined solely by means of the glass electrode—and, corresponding to the salt concentrations employed, the standard

Table 7.

Glass electrode measurements of ethylenediamine containing cadmium salt solutions at 25°.

Calc. with $pk_{enH_2^{++}} = 7.49$, $pk_{enH^+} = 10.17$ ($pH < 9.31$) and $pk_{enH^+} = 10.18$ ($pH > 9{,}31$). $pH_{(st.)} = 2.307$.

$C_{HNO_3} = 0.1006$ and 0.0995 (Nos. 12–14, 16, 17), $C_{KNO_3} = 0.998$

No.	C_{Cd}	C_{en}	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{\alpha_{en}}$	$\bar{n}_{en}$	C'_{en}	$\bar{n}$	p [en]
1	0.0990	0.0625	0.2281	6.166	5.639	1.954	0.0515	0.111	6.637
2	0.0990	0.0787	0.2435	6.427	5.125	1.921	0.0524	0.266	6.123
3	0.0990	0.0915	0.2505	6.545	4.895	1.898	0.0530	0.389	5.892
4	0.0990	0.1098	0.2588	6.686	4.622	1.864	0.0540	0.564	5.619
5	0.0988	0.1237	0.2634	6.764	4.472	1.842	0.0546	0.700	5.469
6	0.0986	0.1859	0.2852	7.133	3.781	1.694	0.0594	1.283	4.779
7	0.0990	0.2142	0.2964	7.322	3.444	1.594	0.0631	1.528	4.441
8	0.0987	0.2431	0.3094	7.542	3.071	1.468	0.0685	1.769	4.069
9	0.0990	0.2735	0.3305	7.899	2.521	1.276	0.0789	1.968	3.519
10	0.0990	0.3070	0.3637	8.460	1.794	1.078	0.0934	2.160	2.792
11	0.0990	0.3309	0.3852	8.825	1.383	1.005	0.1000	2.332	2.381
12	0.0989	0.3377	0.3920	8.940	1.260	0.979	0.1016	2.387	2.262
13	0.0989	0.3687	0.4138	9.309	0.874	0.893	0.1114	2.601	1.876
14	0.0989	0.3935	0.4274	9.538	0.650	0.823	0.1209	2.756	1.652
15	0.0990	0.4245	0.4426	9.795	0.389	0.713	0.1412	2.865	1.387
16	0.0989	0.4562	0.4570	10.039	0.144	0.583	0.1707	2.885	1.146
17	0.0989	0.4887	0.4652	10.177	0.003	0.501	0.1985	2.933	1.005

$C_{HNO_3} = 0.0498$, $C_{BaCl_2} = 0.050$, $C_{KNO_3} = 1.050$

No.	C_{Cd}	C_{en}	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{\alpha_{en}}$	$\bar{n}_{en}$	C'_{en}	$\bar{n}$	p [en]
18	0.0495	0.0778	0.2843	7.118	3.809	1.702	0.0292	0.982	5.112
19	0.0495	0.1014	0.2997	7.378	3.347	1.563	0.0318	1.407	4.650
20	0.0495	0.1779	0.4137	9.307	0.876	0.895	0.0556	2.472	2.179

$C_{HNO_3} = 0.1006$, $C_{BaCl_2} = 0.050$, $C_{KNO_3} = 0.998$

No.	C_{Cd}	C_{en}	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{\alpha_{en}}$	$\bar{n}_{en}$	C'_{en}	$\bar{n}$	p [en]
21	0.0496	0.1063	0.2795	7.036	3.960	1.741	0.0578	0.978	4.957

$C_{HNO_3} = 0.0498$, $C_{BaCl_2} = 0.050$, $C_{KNO_3} = 1.05$

No.	C_{Cd}	C_{en}	$E_{(st.)} - E$	pH	$\log \frac{\bar{n}_{en}}{\alpha_{en}}$	$\bar{n}_{en}$	C'_{en}	$\bar{n}$	p [en]
22	0.0495	0.0488	0.2688	6.855	4.299	1.812	0.0275	0.430	5.602
23	0.0495	0.0778	0.2899	7.213	3.637	1.653	0.0301	0.963	4.940
24	0.0495	0.1132	0.3148	7.634	2.923	1.416	0.0351	1.579	4.226

acid solution was the same as in the experiments recorded in Table 4.

The values for the acid-base constants of the ethylenediamine which are used in calculating the auxiliary quantities $\log \frac{\bar{n}_{en}}{\alpha_{en}}$ and $\bar{n}_{en}$ are to be found at the top of the tables. Taking into consideration the trend of the values for pk_{enH^+} in Table 4, we use the value 10.17 for solutions with $pH < 9.3$, and the value 10.18 for solutions with $pH > 9.3$. The values found for the formation function $\bar{n}$ and the ligand exponent p[en] are recorded in the last two columns of Tables 6 and 7; they are plotted against one another in Fig. 2.

b. Discussion.

Fig. 2, besides the formation curves for the zinc and cadmium complexes, shows a couple of the previously determined formation curves for the ethylenediamine systems of the divalent

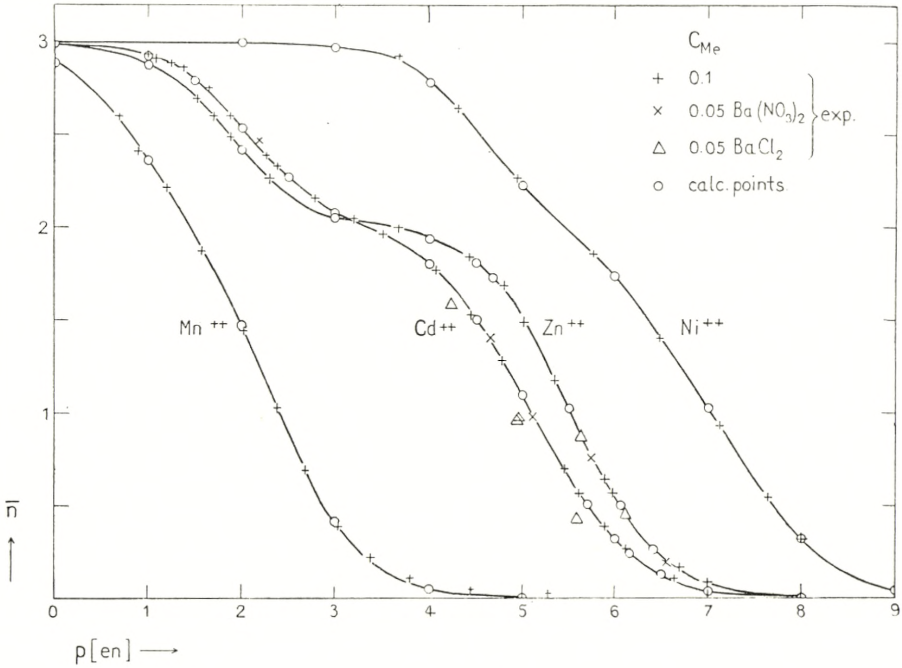

Fig. 2. Formation curves for the tri-ethylenediamine zinc and cadmium ions in 1 N KNO_3 at 25°. For comparison the figure contains the previously determined formation curves for the tri-ethylenediamine manganous and nickel ions in 1 N KCl at 30°.

metal ions of the iron group. The figure shows that both the zinc and the cadmium ion bind up to 3 ethylenediamine molecules, and that the formation curves, as distinct from those of the metal ions of the iron group (most pronounced in the zinc system) are flattened out after the binding of the first 2 ethylenediamine molecules, before the 3rd molecule is taken up. The experimentally determined points corresponding to solutions with a zinc and cadmium concentration of approximately 0.1 molar are in the figure marked by + and for the concentration 0.05 by × and △, all according as the solutions are prepared with barium nitrate or chloride. In the zinc system the experimentally determined points lie almost on one and the same curve, irrespective of the different zinc concentrations and the presence of smaller amounts of chlorine ion. But in the cadmium system the tendency to chloro-complex formation[1] manifests itself, so that the points corresponding to the chloride-containing solutions ($C_{Cl^-} = 0.1$) are distinctly displaced relative to the points corresponding to the completely chloride-free solutions; however, as might be expected in the case of 1-nuclear complexes, there is no dependence on the cadmium concentration.

In the upper part of the formation curves the points are not so nicely placed (a couple of zinc points lie close to the cadmium curve), but this circumstance is associated with the fact that the formation curve in this range is rather sensitive to errors in the hydrogen ion concentration and the values used for the acid-base constants of the ethylenediamine. For the value of the calculation it is an advantage to keep the concentration of the acid-base buffer system small in proportion to that of the complex system, but the nitric acid concentrations 0.1 and 0.05 are chosen with regard to the circumstance that still smaller acid concentrations make the solutions less defined and more basic, with all ensuing drawbacks; for one thing, the danger of hydroxo-complex formation is increased.[2]

It will be seen that the complex formation is almost complete at p[en] about 1, *i. e.* at ethylenediamine concentrations where it is still permissible to reckon with proportionality between concentration and activity.

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[1] Cf. IV, p. 159.

[2] Cf. Grossmann and Schück, Zeitschr. anorg. Chem. **50** (1906) 9.

In the calculation of $\bar{n}$ and p[en] we have assumed that the complex-bound ethylenediamine does not exert any basic function. This assumption is undoubtedly satisfied since the whole course of the curve towards $\bar{n} = 2$ and 3 indicates that all the ethylenediamine is bound "chelate".[1]

4. Calculation of the complexity constants.

The three consecutive complexity constants k_1, k_2, and k_3 of the complex systems examined are defined by the expression

$$k_n = \frac{[\mathrm{Me\ en}_n]}{[\mathrm{Me\ en}_{n-1}]\,[\mathrm{en}]}, \quad n = 1, 2, 3 \tag{14}$$

The 3rd consecutive complexity constant, owing to the flattened shape of the formation curve after the binding of the first 2 ethylenediamine molecules, is almost independent of the first 2 constants, and may therefore with good approximation be computed from each of the points of the curve with $\bar{n} > 2$ by the equation

$$\log k_3 = p[\mathrm{en}] + \log \frac{\bar{n} - 2}{3 - \bar{n}}. \tag{15}$$

Using the experimentally determined values for the ligand exponent and the formation function within the range $\bar{n} = 2.3$—2.7, we calculate with the aid of (15) the following values for $\log k_3$ in the zinc system:

No. (in Tab. 6)	p[en]	$\bar{n}$	$\log k_3$
11	2.299	2.266	1.858
12	1.883	2.484	1.855
13	1.700	2.599	1.874
14	1.527	2.694	1.883
—	1.855	2.500	1.855

and for $\log k_3$ in the cadmium system:

No. (in Tab. 7)	p[en]	$\bar{n}$	$\log k_3$
11	2.381	2.332	2.097
12	2.262	2.387	2.062
20	2.179	2.472	2.130
13	1.876	2.601	2.054
—	2.07	2.500	2.07

---

[1] Cf. IV, p. 216.

It is seen that the calculated values do not deviate much from one another.

The course of the formation curve up to $\bar{n} = 2$ is almost independent of the 3rd constant, and the first 2 constants may therefore with good approximation be calculated from the ligand exponent and the slope of the curve

$$\triangle = \frac{d\bar{n}}{d \ln [en]} = -0.4343 \frac{d\bar{n}}{dp[en]}$$

for $\bar{n} = 1$. The relation between the particular quantities is easily found to be[1]

$$\left.\begin{aligned} \log k_1 &= p[en]_{\bar{n}=1} + \log \frac{2-2\triangle}{\triangle} \\ \log k_2 &= p[en]_{\bar{n}=1} - \log \frac{2-2\triangle}{\triangle}. \end{aligned}\right\} \quad (16)$$

The ligand exponent for a series of rounded-off values of $\bar{n}$ is given in Table 8. The slope of the formation curves, $\triangle_{\bar{n}=1}$ was found to be 0.438 and 0.379 in the zinc and the cadmium systems, respectively. The sets of constants calculated by means of (15) and (16) from $\triangle$ and the graphically interpolated ligand exponents for $\bar{n} = 1$ and 2.5 are recorded in the upper row of Table 9.

In order to check the correctness of the constants thus found and the accuracy of the measurements, a calculation was also made of the sets of constants satisfying the graphically interpolated values for the ligand exponent corresponding to $\bar{n} = 0.5$, 1.5, and 2.5, and for $\bar{n} = 0.25$, 1.75, and 2.5. The calculation

Table 8. Graphically interpolated values for the ligand exponent and calculated values of the formation function.

$\bar{n} =$	0.25	0.50	1.00	1.50	1.75	2.50
Zn: p[en]	6.42	6.06	5.525	5.005	4.68	1.855
Cd: p[en]	6.155	5.71	5.105	4.50	4.11	2.07
Zn: $\bar{n}$ (calc.)	0.263	0.498	1.010	1.507	1.724	2.502
Cd: $\bar{n}$ (calc.)	0.241	0.505	1.004	1.504	1.740	2.498

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[1] See IV, pp. 24 ff.

Table 9. Calculated values for the consecutive complexity constants in the zinc and cadmium ethylenediamine systems.

	$\log k_1$		$\log k_2$		$\log k_3$	
	Zn	Cd	Zn	Cd	Zn	Cd
△ etc.	5.935	5.620	5.115	4.590	1.855	2.07
$\bar{n} = 0.5$ etc.......	5.927	5.622	5.138	4.584	1.856	2.074
$\bar{n} = 0.25$ etc......	5.884	5.651	5.213	4.596	1.856	2.074
"Mean"	5.92	5.63	5.15	4.59	1.85	2.07

was carried out as a successive approximation of the constants determined by means of (15) and (16). For the approximation we used the previously derived formula[1]

$$k_n = \frac{1}{[\mathrm{en}]} \cdot \frac{\displaystyle\sum_{t=0}^{t=n-1} \frac{\bar{n} - n + 1 + t}{[\mathrm{en}]^t k_{n-1} k_{n-2} \cdots k_{n-t}}}{\displaystyle\sum_{t=0}^{t=3-n} (n - \bar{n} + t)[\mathrm{en}]^t k_{n+1} k_{n+2} \cdots k_{n+t}}, \qquad (17)$$

where the parameters are to run through all whole values between the limits fixed. As early as after one, or at the most two, insertions in (17) the constants do not change by further insertion. The constants thus calculated are recorded in the 2nd and 3rd row in Table 9.

A comparison of the constants determined by different methods shows that the 3rd constant calculated from (15), as one would expect, is practically unchanged by the successive approximation, and that the values for $\log k_1$ and $\log k_2$ calculated from (16) are in very nice agreement with the values calculated by means of the ligand exponents for $\bar{n} = 0.5$ and 1.5. The agreement with the constants calculated from the ligand exponents for the more extremely located points corresponding to $\bar{n} = 0.25$ and 1.75, however, is less satisfactory especially as regards one of the zinc constants. All the calculated constants being considered, the bottom row of Table 9 shows the sets of constants which presumably get the closest to satisfying the whole experimental material.

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[1] In the formulae (4) and (5) in IV, pp. 37 and 38, there is an unfortunate misprint, which is easily corrected by comparison with the above formula (17).

Knowledge of the complexity constants permits us to calculate the formation function as well as the degrees of formation for the individual complexes

$$\alpha_n = \frac{[\mathrm{Me\,en}_n]}{C_{\mathrm{Me}}} \tag{18}$$

at any arbitrary concentration of ethylenediamine. If we denote the product of the constants $k_1 k_2 \cdots k_n$ by K_n, and put $K_0 = 1$, the following will apply, as readily demonstrated[1]:

$$\bar{n} = \frac{\sum_0^3 n\, K_n\, [\mathrm{en}]^n}{\sum_0^3 K_n\, [\mathrm{en}]^n} \tag{19}$$

$$\alpha_n = \frac{K_n\, [\mathrm{en}]^n}{\sum_0^3 K_n\, [\mathrm{en}]^n} \tag{20}$$

$$\sum_0^3 \alpha_n = 1 \quad \text{and} \quad \sum_0^3 n\,\alpha_n = \bar{n} \tag{21}$$

By means of (19)—(21) and the constants found, the formation function and the degrees of formation in both the zinc and the cadmium systems are calculated for a series of ethylenediamine concentrations. The results are recorded in Table 10. The formation function is moreover calculated with the use of the graphically interpolated values for the ligand exponent corresponding to rounded-off values of $\bar{n}$. The values thus determined for the formation function are recorded in Table 8; it is seen that they reproduce the experimental data satisfactorily. This is also seen from Fig. 2, where all the calculated $\bar{n}$-values are plotted on the experimentally determined formation curves.

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[1] Cf. IV, pp. 27 ff.

Table 10.

Distribution of the zinc and cadmium ion on the different metal ethylenediamine ions in 1 N potassium nitrate at 25°.

1. Distribution of the zinc ion calculated with:
$\log K_1 = 5.92$, $\log K_2 = 11.07$, $\log K_3 = 12.93$

p [en]	α_0	α_1	α_2	α_3	$\bar{n}$
0	0	0	0.014	0.986	2.987
1	0	0	0.121	0.879	2.877
2	0	0	0.580	0.420	2.419
3	0	0.007	0.927	0.067	2.061
4	0	0.066	0.927	0.007	1.940
5	0.048	0.395	0.557	0	1.511
6	0.514	0.427	0.060	0	0.548
7	0.922	0.077	0.001	0	0.079
8	0.992	0.008	0	0	0.008

2. Distribution of the cadmium ion calculated with:
$\log K_1 = 5.63$, $\log K_2 = 10.22$, $\log K_3 = 12.29$

p [en]	α_0	α_1	α_2	α_3	$\bar{n}$
0	0	0	0.008	0.991	2.991
1	0	0	0.078	0.922	2.922
2	0	0.001	0.459	0.540	2.538
3	0	0.023	0.874	0.103	2.080
4	0.005	0.202	0.784	0.009	1.798
5	0.144	0.616	0.240	0	1.096
6	0.693	0.296	0.012	0	0.319
7	0.959	0.041	0	0	0.041
8	0.996	0.004	0	0	0.004

A graphical presentation of the distribution of the metal ions on the particular complex ions as a function of p [en] is given in Fig. 1 (see p. 6).

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