Metal Ammine Formation in Solution. XXIII. Stability Constants of Protonated Non- and Partly-chelated Complexes in the Cadmium 1,2-Ethanediamine System

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The cadmium 1,2-ethanediamine system was examined at 25 °C employing glass and Cd,Hg-electrode measurements in a 3 M (Na,H)ClO$_4$ medium with initial concentrations of HClO$_4$ varying from 0.01 to 1 M. The cumulative stability constants for the chelated complexes were determined from pH-titrations with low initial acid concentration, and the following constants were obtained: Cd en^{2+}, $\beta_{1,0}=10^{6.21}$; Cd en$_2$$^{2+}$, $\beta_{2,0}=10^{11.64}$; Cd en$_3$$^{2+}$, $\beta_{3,0}=10^{14.38}$. These constants were used to determine the stability constants for the protonated species from Cd,Hg-electrode measurements on solutions with high initial acid concentration (1 M). In this way the following values for the cumulative constants for the three most important species were obtained: Cd en H^{3+}, $\beta_{0,1}=10^{1.70}$; Cd en (en H)$^{3+}$, $\beta_{1,1}=10^{7.88}$; Cd en$_2$ (en H)$^{3+}$, $\beta_{2,1}=10^{12.23}$.

It was shown by Jannik Bjerrum [1] in 1941 that the successive formation constants for some 1,2-ethanediamine complexes of some metal-ions could be determined by pH-titrations of the acid metal salt solutions with the diamine. The procedure involves the tacit assumption that the formation of protonated non-chelate species can be neglected. In 1945 the method was applied by Bjerrum and Andersen[2] in a study of the zinc and cadmium ethanediamine systems, and in the following years many diamine systems were studied making this assumption.[3] Schwarzenbach and Szilard [4] have proven the existence of Cd(tnH)$^{3+}$ in the cadmium 1,2-propanediamine system, but for the more stable ethanediamine complexes with octahedral, tetrahedral or planar configuration it was assumed to be correct to neglect non-chelate complex formation. This is clearly not the case for the complexes formed with silver(I) and mercury(II) ions, with linear configuration, for which it has been shown [5,6] that ethanediamine is bound mainly as a monodentate ligand. However, in polarographic studies Biernat and Wilgocki [7–9] have shown that non-chelate complexes are also present to a great extent in the cadmium 1,2-diamine systems when the complex formation takes place under conditions where the concentration of the monoprotonated diamine is much higher than that of the diamine. The existence of complexes with monodentate bound ligands in zinc diamine systems was demonstrated similarly.[10] In the present study the cadmium 1,2-ethanediamine system has been studied by glass and Cd,Hg-electrode measurements in a 3 M (Na,H)ClO$_4$ medium. The stability constants for the chelate complexes have been obtained from measurements involving a low initial acid concentration, and the stability constants for the three most important protonated complexes Cd(enH)$^{3+}$, Cd en (enH)$^{3+}$ and Cd en$_2$(enH)$^{3+}$ have been determined from measurements involving a high initial acid concentration.

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EXPERIMENTAL

Reagents and solutions. All reagents were of analytical grade and were used without further purification. The ethylenediamine (Fluka, *puriss, p.a.*) was distilled before use. The various solutions were prepared in volumetric flasks by weighing or pipetting from analyzed stock solutions of cadmium perchlorate, sodium perchlorate, perchloric acid and ethylenediamine.

Glass electrode measurements were performed in a jacketed vessel with thermostatted water flow. pH ($=-\log [H^+]$) was measured relative to that of standard $HClO_4$-solutions (pH ~3) in 3 M $NaClO_4$. Selected Radiometer glass electrodes (G 202 C for pH <9 and G 202 B for pH >9) were used, both having nearly the theoretical pH-dependence. The potentiometer used was a Radiometer PHM 52 Digital pH-Meter, the mV-scale being preferred to the direct reading pH-scale. Sodium chloride calomel electrodes (1 and 0.05 M) prepared according to Gjaldbæk[11] and in electrode vessels of the type introduced by Lewis *et al.*[12] were used as reference electrodes.

Cd,Hg-electrode measurements were performed in a closed jacketed vessel with electrical connection to the reference electrode and with in- and outlet for nitrogen. A melted-in platinum wire provided contact to the liquid amalgam placed in a cavity in the bottom of the cell. The cadmium amalgam was prepared according to Szilard[13] by dissolving granulated cadmium metal in mercury placed in a 1 M perchloric acid solution under stirring at about 80 °C. The amalgam was stored under 10^{-3} M $HClO_4$. Dissolved oxygen was removed from the solution to be examined by bubbling with nitrogen before the amalgam was added to the cell. The nitrogen was purified by passing it consecutively through bubblers with spiral grooved fitted inner-tubes containing a concentrated solution of catechol in 50 % KOH and an acidic chromium(II) sulfate solution containing amalgamated zinc.[14] Cadmium amalgam potentials in oxygen-free solutions are well-defined and independent of the cadmium concentration in the two-phase range between 6 and 13 % of cadmium.[15] Our measurements of the cadmium ion concentration were performed with both a two-phase and (in most cases) a homogeneous 2 % amalgam with exactly the same result.

RESULTS

The *acid-dissociation constants for the 1,2-ethanediammonium ion in 3 M (Na,H)ClO4.* The acid dissociation constants, $K_{en\ H_2^{2+}}$ and $K_{en\ H^+}$,

Table 1. Acid-base constants of 1,2-ethanediamine in 3 M (Na,H)ClO$_4$ with $[H^+]_o=0.02$ and 1 M at 25 °C.

C_{NaClO_4}	C_{HClO_4}	C_{en}	pH	p$K_{en\ H_2^+}$
2.98	0.02136	0.01365	7.843	7.959
2.98	0.02129	0.01429	7.972	7.958
			av.	7.95±0.01
2.00	1.0235	0.6648	7.855	7.927
2.00	1.0231	0.6717	7.884	7.927
			av.	7.93±0.01
				p$K_{en\ H^+}$
2.98	0.02126	0.03850	10.692	10.799
2.98	0.02114	0.04324	10.784	10.782
			av.	10.79±0.01
1.95	1.0551	1.4435	10.348	10.790
2.00	1.0257	2.0083	10.820	10.840
			av.	10.81±0.01
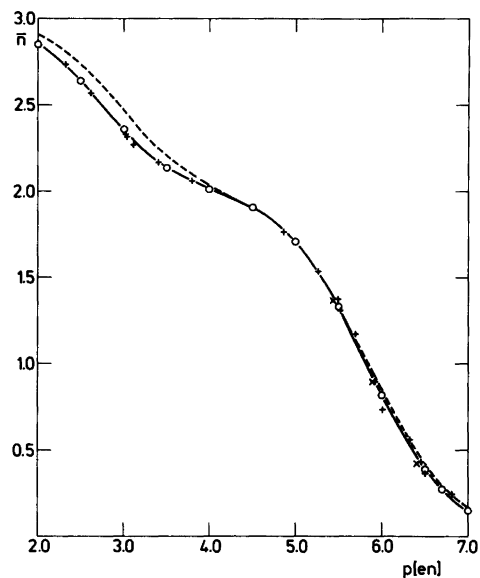
Fig. 1. Formation curve ($\bar{n}$ *versus* p[en]) for the Cd^{2+}, en system in 3 M $NaClO_4$ at 25 °C. Experimental results with $C_{Cd(ClO_4)_2}\cong0.02$ M, $C_{HClO_4}\cong0.02$ M (+) and with $C_{Cd(ClO_4)_2}\cong0.10$ M, $C_{HClO_4}\cong0.01$ M (×). The full curve (O) is calculated with the constants derived from the pH-measurements ($\beta_{1,0}=10^{6.21}$, $\beta_{2,0}=10^{11.64}$, $\beta_{3,0}=10^{14.38}$) and the dotted curve with constants derived from the Cd,Hg-measurements ($\beta_{1,0}=10^{6.28}$, $\beta_{2,0}=10^{11.65}$, $\beta_{3,0}=10^{14.61}$).

Table 2. Results of glass and Cd,Hg-electrode measurements in ~3 M $NaClO_4$ at 25 °C. Data for 10 of 21 solutions studied. $C_{NaClO_4}=3.00-C_{HClO_4}-2C_{Cd(ClO_4)_2}$. $pK_{en\ H_2}=7.95$, $pK_{en\ H}=10.79$.

No.	C_{HClO_4}	$C_{Cd(ClO_4)_2}$	C_{en}	pH	$\bar{n}_{en}$	p[en]
1	0.02124	0.02002	0.01866	7.115	1.873	6.512
2	0.02121	0.02003	0.02263	7.213	1.845	6.327
3	0.02127	0.02000	0.02640	7.347	1.800	6.071
4	0.02112	0.02002	0.03888	7.647	1.667	5.519
5	0.02123	0.01999	0.04405	7.791	1.590	5.262
6	0.02122	0.02003	0.04995	8.026	1.455	4.865
7	0.02123	0.02001	0.06377	9.116	1.043	3.402
8	0.02133	0.02007	0.06695	9.379	0.999	3.113
9	0.02137	0.02003	0.07502	9.855	0.908	2.615
10	0.02144	0.02006	0.08105	10.140	0.823	2.322

No.	$\bar{n}_{Cd}$(exp)	$\bar{n}$(calc.) [a]	$\bar{n}$(calc.) [b]	$X_{(exp)}$	$X_{(calc.)}$ [a]	$X_{(calc.)}$ [b]
1	0.365	0.378	0.412	1.68	1.54	1.63
2	0.558	0.515	0.549	2.08	1.86	2.00
3	0.730	0.742	0.769	2.86	2.65	2.94
4	1.309	1.303	1.286	11.0	9.91	10.9
5	1.535	1.535	1,537	24.9	22.9	25.4
6	1.766	1.776	1.750	119	105	112
7	2.169	2.170	2.245	10.4×10^4	8.4×10^4	9.6×10^4
8	2.271	2.294	2.408	4.7×10^5	3.7×10^5	4.5×10^5
9	2.569	2.570	2.688	8.6×10^6	6.0×10^6	8.5×10^6
10	2.738	2.728	2.813	5.1×10^7	3.6×10^7	5.4×10^7

[a] Calc. with $\log \beta_{1,0}=6.21$, $\log \beta_{2,0}=11.64$, $\log \beta_{3,0}=14.38$. [b] Calc. with $\log \beta_{1,0}=6.28$, $\log \beta_{2,0}=11.65$, $\log \beta_{3,0}=14.61$.

for the 1,2-ethanediammonium ion were determined in the same way as in previous studies.[1,2] The results of some of the determinations are shown in Table 1. The data show in a convincing way that substitution of 1 M $NaClO_4$ with 1 M ($\frac{1}{2}$ en H_2, en H)ClO_4 has practically no influence on the values of $pK_{en\ H_2^{2+}}$ and $pK_{en\ H^+}$. It is therefore reasonable to assume that this change in medium also has no influence on the stability constants.

Estimation of the stability constants $\beta_{1,0}$, $\beta_{2,0}$ and $\beta_{3,0}$ for the three chelate complexes in 3 M $NaClO_4$. These measurements were made under conditions (low initial acid concentration) where the concentrations of the protonated non-chelated complexes could be assumed to be negligible. Some of the results are shown in Table 2. The calculations based on the glass electrode measurements were made as described previously.[1,2] $\bar{n}_{en}$ denotes the average number of protons bound per diamine and $\bar{n}_{Cd}$ the average number of diamine ligands bound to cadmium. p[en] is the negative exponent of the free diamine

concentration. The agreement between the experimental results (with C_{Cd} 0.02, C_{HClO_4} 0.02 M (+), and with C_{Cd} 0.10, C_{HClO_4} 0.01 M (×)) and the formation curve derived from the calculated constants is shown in Fig. 1. Another set of stability constants was calculated from the measurements of the cadmium ion concentrations by means of eqn. (1)

$$X = \frac{C_{Cd}}{[Cd^{2+}]} = 1+\beta_{1,0}[en]+\beta_{2,0}[en]^2+\beta_{3,0}[en]^3 \tag{1}$$

employing the values of the free diamine concentration determined from pH-measurements. The formation curve derived from these constants (the dotted curve in Fig. 1) shows some deviation from the formation curve calculated solely on the basis of the pH-measurements. A plausible explanation for this is that the Cd,Hg-electrode shows deviations from Nernst' law for $[Cd^{2+}]\lesssim10^{-6}$ M.[4] This corresponds in our case to X-values higher than ~10^5 and $\bar{n}\geq2$, and explains the deviation between the two formation curves

Table 3. Results of glass and Cd,Hg-electrode measurements in 3 M (H,Na)ClO$_4$ with $C_{HClO_4}=1.007$ (Nos. 1–8, 10, 11), 1.013 (Nos. 9, 12), $C_{Cd(ClO_4)_2}=0.00503$ M and $C_{NaClO_4}=3.00-C_{HClO_4}-2$ $C_{Cd(ClO_4)_2}$. $pK_{en\ H_2}=7.93$, $pK_{en\ H}=10.81$.

No.	C_{en}	pH	p[en]	p[en H$^+$]	X_{exp}	Δ [a]	Δ [b]
1	0.5095	5.938	7.164	2.292	1.324	1.21	1.19
2	0.5170	6.330	6.383	1.904	2.647	1.90	1.78
3	0.5182	6.381	6.282	1.853	3.614	2.58	2.52
4	0.5250	6.559	5.929	1.678	6.282	3.77	3.42
5	0.5281	6.640	5.769	1.599	9.716	5.69	5.18
6	0.5347	6.793	5.467	1.451	24.73	14.1	13.0
7	0.5415	6.975	5.111	1.276	75.32	36.5	33.6
8	0.5865	7.433	4.236	0.859	2.728×10^3	1.11×10^3	1.03×10^3
9	0.6129	7.570	3.981	0.741	10.041×10^3	4.83×10^3	4.50×10^3
10	0.6607	7.815	3.549	0.554	8.656×10^4	4.59×10^4	4.12×10^4
11	0.6778	7.876	3.445	0.511	1.565×10^5	0.89×10^5	0.79×10^5
12	0.7097	8.001	3.237	0.426	3.831×10^5	1.89×10^5	1.53×10^5

[a] Calc. with $\log \beta_{1,0}=6.21$, $\log \beta_{2,0}=11.64$, $\log \beta_{3,0}=14.38$.   [b] Calc. with $\log \beta_{1,0}=6.28$, $\log \beta_{2,0}=11.65$, $\log \beta_{3,0}=14.61$.

found at low p[en]-values. The two sets of constants were used to calculate $\bar{n}$ and X for each of the ten values in Table 2, and in the lower part of the table they are compared with the experimentally determined values.

Estimation of the stability constants for three of the protonated complexes. Apart from the chelate complexes Cd en^{2+}, Cd en$_2{}^{2+}$ and Cd en$_3{}^{2+}$, it is most reasonable to assume the existence, among the numerous possibilities, of the following protonated species: Cd en H^{3+}, Cd en (en H)$^{3+}$ and Cd en$_2$ (en H)$^{3+}$ at high 1,2-ethaneammonium ion concentrations. It should then be possible knowing the stability constants for the chelated complexes to estimate the stability constants for the protonated complexes in the more acidic medium using eqn. (2)

Table 4. Results of calculations of stability constants for the protonated complexes.

	$\beta_{0,1}$	$\beta_{1,1}$	$\beta_{2,1}$
With Δ [a]	52±3	$(7.8\pm0.5)\times10^7$	$(1.78\pm0.02)\times10^{12}$
With $\beta_{0,2}\equiv1000$	45±3	$(7.1\pm0.5)\times10^7$	$(1.80\pm0.02)\times10^{12}$
With Δ [b]	48±3	$(7.3\pm0.5)\times10^7$	$(1.59\pm0.02)\times10^{12}$
Av. Δ [a] and Δ [b]	50	7.5×10^7	1.7×10^{12}

Table 5. Comparison of cadmium(II)–ethanediamine and ammonia stability constants.

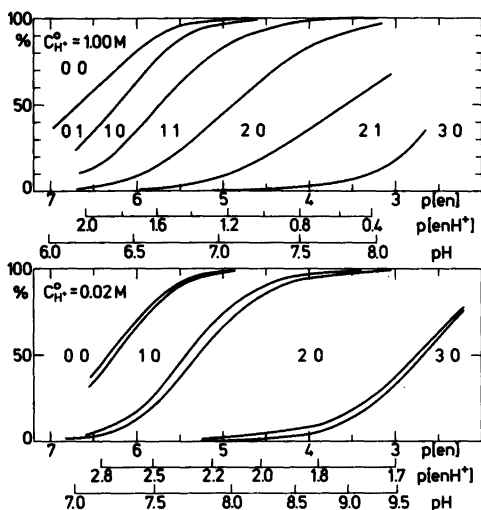| Cd^{2+},en(en H$^+$) 3 M, 25 °C	Cd^{2+},NH$_3$ [1] 2 M, 25 °C	Found
$\log \beta_{0,1}=1.70$	$\log K_1=2.69$	$\log (K_1/\beta_{0,1})=0.99$
$\log \beta_{1,0}=6.21$	$\log K_2=2.14$	
$\log \beta_{1,1}=7.88$	$\log K_3=1.48$	$\log (\beta_{1,1}/\beta_{1,0})=1.67$
$\log \beta_{2,0}=11.64$	$\log K_4=0.97$	
$\log \beta_{2,1}=12.23$	$\log K_5=-0.32$	$\log (\beta_{2,1}/\beta_{2,0})=0.59$
$\log \beta_{3,0}=14.38$	$\log K_6=-1.66$	

Fig. 2. Distribution of the six cadmium(II)–ethanediamine complexes at 25 °C. The ranges of existence of the six complexes from monoamine to hexaamine are plotted *versus* p[en]. The abscissa also shows the corresponding values of p[en H$^+$] and pH. *Upper figure.* In 3 M (NaH)ClO$_4$ for solutions with C_{Cd} 0.005, C_{HClO_4} 1.00, and C_{en} 0.01–0.1 M. *Lower figure.* In 3 M NaClO$_4$ for solutions with C_{Cd} 0.01–0.02, C_{HClO_4} 0.01–0.02, and C_{en} 0.01–0.1 M. The distribution curves in both figures are calculated with: $\beta_{0,1}=10^{1.70}$, $\beta_{1,0}=10^{6.21}$, $\beta_{1,1}=10^{7.88}$, $\beta_{2,0}=10^{11.64}$, $\beta_{2,1}=10^{12.23}$, $\beta_{3,0}=10^{14.38}$.

$$\Delta = X - \beta_{1,0}[en] - \beta_{2,0}[en]^2 - \beta_{3,0}[en]^3 =$$
$$1 + \beta_{0,1}[en\,H^+] + \beta_{1,1}[en][en\,H^+] + \beta_{2,1}[en]^2[en\,H^+]$$
$$(2)$$

and making the very plausible assumption that the stability constants in 3 M NaClO$_4$ are practically unchanged when 1 M NaClO$_4$ is replaced with 1 M ($\frac{1}{2}$ en H$_2$,en H)ClO$_4$.

In the chosen medium with $C^\circ_{HClO_4}=1$ M the applied cadmium concentrations are so small compared with the concentrations of the 1,2-ethaneammonium ions that p[en] and p[en H$^+$] can be calculated directly from the pH-measurements irrespective of the fact that some of the protons are bound to the complexes. Under these circumstances it is not possible to calculate $\bar{n}_{Cd}$ from pH measurements and $X=C_{Cd}/[Cd^{2+}]$ is thus the sole basis for the calculations. The data for twelve of the solutions examined are shown in Table 3. The values of Δ^a and Δ^b were calculated knowing $\beta_{1,0}$, $\beta_{2,0}$ and $\beta_{3,0}$. Consequently, twelve equations are at our disposal for determining the three unknown ($\beta_{0,1}$, $\beta_{1,1}$ and $\beta_{2,1}$) of eqn. (2). A computer program was written for the purpose and the calculations were made using both sets of Δ-values. The results of the calculations are shown in Table 4. An attempt was also made to calculate $\beta_{0,2}$ and $\beta_{1,2}$ at the same time, but this placed too heavy a load on the data, and realistic values for these constants could therefore not be

Table 6. Chelation effects in metal(II)–ethanediamine systems relative to ammonia.

	Cd^{2+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}
log $\beta_{1,0}(en)/K_1(NH_3)$	3.0	3.6	6.6	4.7	3.8
log $\beta_{2,0}(en)/\beta_2(NH_3)$	6.5	6.4	12.4	8.9	7.1

Table 7. Stability constants for the chelated copper(II)–ethanediamine complexes [17] supplemented with empirically selected values for the protonated complexes.

Cu^{2+},en(en H$^+$) 1.3 M, 25 °C	Cu^{2+},NH$_3$ [1] 2 M, 25 °C	Assumption
log $\beta_{0,1}=$ 3.20	log $K_1=4.22$	log $(K_1/\beta_{0,1})\cong1.0$
log $\beta_{1,0}=10.75$	log $K_2=3.57$	
log $\beta_{1,1}=13.75$	log $K_3=2.96$	log $(\beta_{1,1}/\beta_{1,0})\cong3.0$
log $\beta_{2,0}=20.03$	log $K_4=2.20$	

Table 8. Stability constants for the chelated nickel(II)–ethanediamine complexes [18] supplemented with empirically selected values for the protonated complexes.

Ni^{2+},en(en H^+) 1.3 M, 25 °C	Ni^{2+},NH_3 [1] 2 M, 25 °C	Assumption
$\log \beta_{0,1}= 1.80$	$\log K_1=2.84$	$\log (K_1/\beta_{0,1})\cong1.0$
$\log \beta_{1,0}= 7.66$	$\log K_2=2.28$	
$\log \beta_{1,1}= 9.16$	$\log K_3=1.77$	$\log (\beta_{1,1}/\beta_{1,0})\cong1.5$
$\log \beta_{2,0}=14.06$	$\log K_4=1.23$	
$\log \beta_{2,1}=14.86$	$\log K_5=0.79$	$\log (\beta_{2,1}/\beta_{2,0})\cong0.8$
$\log \beta_{3,0}=18.61$	$\log K_6=0.07$	

obtained. On the other hand, $K_{0,2}$, the constant for the uptake of the second en H^+-ligand by Cd en H^{3+}, can be estimated empirically to be <20, corresponding to $\beta_{0,2}<1000$. Table 4 demonstrates that the introduction of $\beta_{0,2}\equiv1000$ in the calculations has very little influence on values of the other constants. It is therefore understandable that the data cannot be stretched to calculate stability constants for other than the three monoprotonated constants.

Fig. 2 shows the results of a calculation of the ranges of existence of the various cadmium species in the 3 M perchlorate solutions with different initial acid concentrations. The figure shows that formation of the protonated complexes is very considerable in the solutions with $C^\circ_{HClO_4}=1$ M and strongly suppressed in the solutions with $C^\circ_{HClO_4}$ as low as 0.02 M. This confirms on the whole our assumption that $\beta_{1,0}$,

$\beta_{2,0}$ and $\beta_{3,0}$ can be determined at low initial acid concentration with only little interference from the formation of protonated complexes.

DISCUSSION OF RESULTS

The cumulative constants $(\beta_{n,1})$ found for the uptake of en- and en H^+-ligands are compared in Table 5 with the consecutive constants (K_n) for the corresponding cadmium-ammonia system.[1] It can be read from the table that the first en H^+-ligand is about 10 times more weakly bound to the cadmium ion than the first ammonia molecule. A decrease in affinity of this order of magnitude is also found in the corresponding silver(I) systems for which $\log K_1$ is found to be 3.40 [1] in the ammonia system at 20 °C whereas $\log \beta_{0,1}$ has the value 2.35 in the 1,2-ethanediamine system at the same temperature.[16]
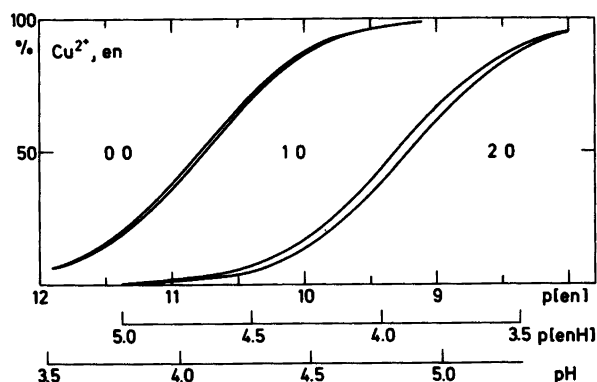

Fig. 3. Distribution of the complexes Cu(en H)$^{3+}$, Cu en^{2+}, Cu en (en H)$^{3+}$ and Cu en$_2^{2+}$ estimated from the data of Bjerrum and Nielsen [17] ($\beta_{1,0}=10^{10.75}$, $\beta_{2,0}=10^{20.03}$) for solutions with: C_{KNO_3} 1.00, C_{Cu} 0.10, C_{HNO_3} 0.10 and C_{en} varying from 0.06 to 0.3 M at 25 °C. The stability constants for Cu (en H)$^{3+}$ and Cu en (en H)$^{3+}$ were assumed empirically to have the values: $\beta_{0,1}=10^{3.20}$ and $\beta_{1,1}=10^{13.75}$.
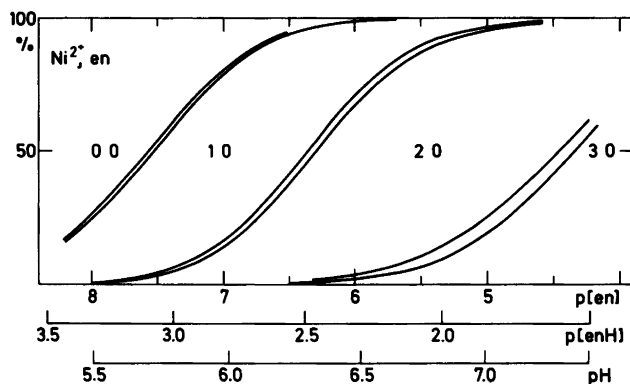
Fig. 4. Distribution of the six nickel(II)–ethanediamine complexes estimated from the data of Poulsen and Bjerrum [17] ($\beta_{1,0}=10^{7.66}$, $\beta_{2,0}=10^{14.06}$, $\beta_{3,0}=10^{18.61}$) for solutions with C_{KNO_3} 1.00, C_{Cu} 0.10, C_{HNO_3} 0.10 and C_{en} varying in the range 0.08–0.3 M at 25 °C. The stability constants for Ni(en H)$^{3+}$, Ni en (en H)$^{3+}$ and Ni en$_2$ (en H)$^{3+}$ were assumed empirically to have the values $\beta_{0,1}=10^{1.80}$, $\beta_{1,1}=10^{9.16}$ and $\beta_{2,1}=10^{15.06}$.

The influence of the positive charge on the protonated ligand ($NH_2CH_2CH_2NH_3{}^+$) is also of the same order in the Hg(II) systems.[1,6] The constant for the binding of an en H$^+$-ligand to Cd en^{2+} ($=\beta_{1,1}/\beta_{1,0}$) is seen to have a relatively high value comparable with the values for K_2 and K_3 in the ammonia system. This is tantamount to a considerable stabilization of the mixed complex Cd en (en H)$^{3+}$ relative to Cd(NH$_3$)$_3{}^{2+}$. The cadmium ion has only a very small affinity for more than four ammonia molecules [1] and it is therefore remarkable that the constant for binding of en H$^+$ to Cd en$_2{}^{2+}$ (log $\beta_{2,1}/\beta_{2,0}=0.59$) has a relatively high value. The reason for this must be that Cd en$_2{}^{2+}$, which has been shown recently [20] to have tetrahedral configuration, rather easily converts to octahedral configuration with Cd en$_2$ (en H)$^{3+}$ as an intermediate.

In the work of Jannik Bjerrum and coworkers on the determination of the stability constants for metal(II)−1,2-ethanediamine complexes [1,2,17–19] in 1.3 M chloride or nitrate solutions with the initial acid concentration as high as 0.10 M, the influence of protonated complexes has been neglected. It therefore has some interest to use the knowledge acquired for the cadmium system to estimate the error introduced by this omission. The chelation effects in the copper(II)– and nickel(II)–1,2-ethanediamine systems relative to the corresponding ammonia systems are higher than in the cadmium systems (see Table 6). It

should therefore be expected that the formation of protonated complexes is of little importance in these systems. The basis for estimating the constants for the protonated complexes in the copper(II) and nickel(II) systems is given in Tables 7 and 8, and in Figs. 3 and 4 the probable ranges of existence of all of the species are calculated. The conclusion which can be drawn from the figures is that the needed correction to the previously determined stability constants for the copper(II)– and nickel(II)–ethanediamine systems are so small that they have kept their value within the accuracy of the determinations.

REFERENCES

1. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution,* P. Haase and Son, Copenhagen 1941, reprinted 1957.
2. Bjerrum, J. and Andersen, P. K. *Dan. Vidensk. Selsk., Mat.-Fys. Medd. 22* (1945) No. 7.
3. Sillen, L. G. and Martell, A. E. *Chem. Soc. Spec. Publ. 17* (1964), *Suppl. 25* (1970).
4. Schwarzenbach, G. and Szilard, I. *Helv. Chim. Acta 45* (1962) 1222.
5. Schwarzenbach, G. *Helv. Chim. Acta 35* (1952) 2344.

6. Bjerrum, J. and Larsen, E. *Essays in Coordination Chemistry, Exper. Suppl. 9* (1964) 39.
7. Biernat, J. and Wilgocki, M. *Rocz. Chem. 48* (1974) 1663.
8. Wilgocki, M. *Dissertation,* Wrocław 1976.
9. Wilgocki, M. and Biernat, J. *Rocz. Chem. 51* (1977) 1297.
10. Wilgocki, M. and Biernat, J. *Congress on Polarography,* Prague 1980, Proc. II, p. 191.
11. Gjaldbæk, J. K. *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd. 5* (1924) No. 9.
12. Lewis, G. N., Brighton, T. B. and Sebastian, R. L. *J. Am. Chem. Soc. 39* (1917) 2245.
13. Szilard, I. *Diss.* No. 3218, Zürich 1961.
14. Stone, H. W. *J, Am. Chem. Soc. 58* (1936) 2591.
15. Leden, I. *Diss.,* Lund 1943, p. 34.
16. Schwarzenbach, G. *Helv. Chim. Acta 36* (1952) 23.
17. Bjerrum, J. and Nielsen, E. J. *Acta Chem. Scand. 2* (1948) 297.
18. Poulsen, I. and Bjerrum, J. *Acta Chem. Scand. 9* (1955) 1407.
19. Pecsok, R. L. and Bjerrum, J. *Acta Chem. Scand. 11* (1957) 1419.
20. Fujita, T. and Ohtaki, H. *Bull. Chem. Soc. Jpn. 53* (1980) 930.