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### STABILITY CONSTANTS OF PROTONATED NON-AND PARTLY-CHELATED COMPLEXES IN THE ZINC 1,2-ETHANEDIAMINE SYSTEM

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## STABILITY CONSTANTS OF PROTONATED NON- AND PARTLY-CHELATED COMPLEXES IN THE ZINC 1,2-ETHANEDIAMINE SYSTEM

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Complex formation between Zn(II) ion and 1,2-ethanediamine (en) or 2-aminoethylammonium cation ( $\text{enH}^+$ ) has been studied in 3 M (Na,H)ClO<sub>4</sub> at 25°, by measuring the e.m.f. of glass and Zn(Hg) electrodes. At low initial acid concentration range and relatively high initial Zn(II) concentration the formation of a precipitate (for  $n < 1.9$ ) was observed. From e.m.f. measurements of the solutions with high initial 1,2-ethanediammonium diperchlorate concentrations ( $C_{\text{enH}_2(\text{ClO}_4)_2} = 0.75$  or 0.50 M) and a low initial Zn(II) concentration ( $C_{\text{Zn}(\text{ClO}_4)_2} = 4.79 \times 10^{-3}$  M) the values for the cumulative stability constants of the following complexes were evaluated:  $\text{Zn}(\text{en})^{2+}$ ,  $\beta_{10} = 10^{6.49 \pm 0.02}$ ;  $\text{Zn}(\text{en})_2^{2+}$ ,  $\beta_{20} = 10^{12.44 \pm 0.01}$ ;  $\text{Zn}(\text{en})_3^{2+}$ ,  $\beta_{30} = 10^{14.88 \pm 0.12}$ ;  $\text{Zn}(\text{enH})^{3+}$ ,  $\beta_{01} = 10^{1.03 \pm 0.06}$ ;  $\text{Zn}(\text{en})(\text{enH})^{3+}$ ,  $\beta_{11} = 10^{7.47 \pm 0.13}$ ;  $\text{Zn}(\text{en})_2(\text{enH})^{3+}$ ,  $\beta_{21} = 10^{12.81 \pm 0.03}$ .

### INTRODUCTION

Prior to 1945 Jannik Bjerrum determined stability constants for 1,2-ethanediamine complexes with Mn(II), Fe(II), Co(II), Ni(II) in 1 M KCl<sup>1</sup> and with Cd(II) and Zn(II) in 1.2 M KNO<sub>3</sub>.<sup>2</sup> However, the coexistence of chelated and non-chelated Cd(II) complexes with 1,2-ethanediamine was reported only in 1974 and was based on polarographic studies.<sup>3</sup> Polarographic studies carried out with a large excess of 2-aminoethylammonium cation with respect to 1,2-ethanediamine showed that Zn(II) also forms non-chelated complexes.<sup>4</sup> As shown in our previous studies<sup>5</sup> stability constants for the Cd(en)<sup>2+</sup>, Cd(en)<sub>2</sub><sup>2+</sup>, Cd(en)<sub>3</sub><sup>2+</sup> complexes in 3 M NaClO<sub>4</sub> may be determined on the basis of the average ligand number obtained at a low initial acid concentration, since under such conditions the concentrations of protonated complexes could be assumed to be negligible. It was also shown that at high acid concentration,  $C_{\text{HClO}_4} = 1$  M, the non-chelated Cd(enH)<sup>3+</sup> and partly-chelated Cd(en)(enH)<sup>3+</sup>, Cd(en)<sub>2</sub>(enH)<sup>3+</sup> complexes coexist in equilibrium with the chelated complexes.<sup>5</sup>

In the present study the Zn(II) — 1,2-ethanediamine system has been studied by means of the glass and Zn(Hg) electrodes in 3 M (Na, H)ClO<sub>4</sub>. From glass electrode measurements of solutions involving a low initial acid concentration only the value of log K<sub>30</sub> for the Zn(en)<sub>3</sub><sup>2+</sup> complex has been evaluated. On the basis of measurements at high total concentrations of 1,2-ethanediammonium diperchlorate with respect to the total zinc perchlorate by means of the glass and Zn(Hg) electrodes, the cumulative stability constants for Zn(en)<sup>2+</sup>, Zn(en)<sub>2</sub><sup>2+</sup>, Zn(en)<sub>3</sub><sup>2+</sup>, Zn(enH)<sup>3+</sup>, Zn(en)(enH)<sup>3+</sup> and Zn(en)<sub>2</sub>(enH)<sup>3+</sup> have been determined.

### EXPERIMENTAL

Zinc perchlorate was prepared from ZnO (Analar, BDH) and HClO<sub>4</sub> (G.R., Merck) and then recrystallized from water. The Zn(II) concentration was determined by titration (according to Schwarzenbach<sup>6</sup>) with EDTA (the latter being determined by titration with standard Mg(II) solution). 1,2-ethanediamine (puriss., p.a., Fluka) was redistilled

before use. The concentration of stock 1,2-ethanediamine solution was determined by titration with standard  $\text{HClO}_4$  solution.<sup>1</sup> Stock perchloric acid solution was prepared from 70%  $\text{HClO}_4$  (G.R., Merck) by diluting. The hydrogen ion concentration was determined by titration with standard  $\text{NaOH}$  or *tris*-(hydroxymethyl)aminomethane solution. 1,2-ethanediammonium diperchlorate,  $1,2\text{-enH}_2(\text{ClO}_4)_2$ , was synthesized in the following way. Redistilled 1,2-ethanediamine was dissolved in triply distilled water and then titrated with perchloric acid at low temperature (below  $30^\circ$ ). The 1,2-ethanediammonium diperchlorate solution was concentrated under reduced pressure in a rotary evaporator. Crystals of 1,2-ethanediammonium diperchlorate thus obtained were recrystallized from aqueous ethanol and finally dried under reduced pressure in a desiccator over silica gel. Sodium hydroxide solutions were prepared from a 50%  $\text{NaOH}$  solution ( $\text{NaOH}$ , p.a., POCh, Gliwice) by dilution and standardized against  $\text{HClO}_4$ . The concentration of stock  $\text{NaClO}_4$  (G.R., Merck) solution was determined by titration of the eluate from a cation-exchange column with standard  $\text{NaOH}$  solution. Mercury (A.R., POCh, Gliwice) was redistilled just before use.

The various solutions were prepared in volumetric flasks by weighing or pipetting from stock solutions of zinc perchlorate, sodium perchlorate, perchloric acid, 1,2-ethanediamine or 1,2-ethanediammonium diperchlorate, respectively.

Glass electrode measurements were performed in a jacketted vessel with a thermostatted water flow.  $\text{pH}(= -\log[\text{H}^+])$  was measured with respect to that of standard  $\text{HClO}_4$  solutions ( $\text{pH} \sim 3$ ) in 3 M  $\text{NaClO}_4$ , as previously described.<sup>5</sup> Glass electrodes (Radiometer G 202 C for  $\text{pH} < 9$  and Beckman 39099 for  $\text{pH} > 9$ ) were used, both having nearly a theoretical  $\text{pH}$ -dependence. An Orion Research Digital Ionalyser 701A was used for  $\text{pH}$  and e.m.f. measurements with the  $\text{Zn}(\text{Hg})$  electrode. A silver-silver chloride electrode was prepared according to Brown.<sup>7</sup> The Kawai's half cell<sup>8</sup> was used as a reference electrode ( $\text{Ag}, \text{AgCl}/0.01 \text{ Ag}^+, 3.0 \text{ Na}^+, 3.01 \text{ ClO}_4^-/3.0 \text{ M NaClO}_4$ ). The used potentiometric cell was a closed jacketted  $150 \text{ cm}^3$  vessel which was provided with a J-shape and amalgam electrode,<sup>9</sup> the Kawai's reference half cell,<sup>8</sup> a glass electrode and a glass tube for argon inlet and outlet. The temperature at  $25 \pm 0.1^\circ$  was maintained by means of an ultrathermostat. The zinc amalgam was prepared just before use in an amalgam electrode apparatus<sup>9</sup> by dissolving zinc metal (puriss., p.a. granular, Fluka) in mercury placed in 0.02 M perchloric acid solution with stirring and under argon at about  $50^\circ$ . Zinc content of the amalgam was about 1.5% by weight. Potentials of the zinc amalgam electrode in oxygen-free zinc(II) - ( $\text{NaClO}_4 + \text{enH}_2(\text{ClO}_4)_2$ ) solutions were stable within the accuracy of the measurements ( $\pm 0.1 \text{ mV}$ ) for several hours. The  $\text{Zn}(\text{Hg})$  electrode exhibited very nearly the theoretical Nernstian slope in the test solutions ( $C_{\text{Zn}(\text{ClO}_4)_2} = 0.0005\text{--}0.05 \text{ M}$ ,  $C_{(\text{Na,H})\text{ClO}_4} = 3.0 \text{ M}$ ,  $\text{pH} \lesssim 4.8$ ) under examination. Argon was purified by passing it in turn through a concentrated solution of pyrogallol in 50%  $\text{KOH}$ , acid chromium(II) sulphate solution containing amalgamated zinc<sup>10</sup> and 3 M  $\text{NaClO}_4$ , respectively.

## RESULTS AND DISCUSSION

### *Complex formation at low acid concentration*

The present studies were carried out under similar conditions ( $C_{\text{Zn}(\text{ClO}_4)_2} = 0.02 \text{ M}$ ,  $C_{\text{HClO}_4} = 0.02 \text{ M}$ ) as previously described with  $\text{Cd}(\text{II})$  as the central cation<sup>5</sup> and for  $C_{\text{Zn}(\text{ClO}_4)_2} = 0.10 \text{ M}$  (like the  $\text{Zn}(\text{II}) - \text{en} - 1.2 \text{ M} (\text{K}, \text{H})\text{NO}_3$  system).<sup>2</sup> Calculations of the negative exponent of the free 1,2-ethanediamine concentration ( $\text{p}[\text{en}]$ ) were based upon the acid dissociation constants for the 1,2-ethanediammonium cation ( $\text{p}K_{\text{enH}_2^{2+}} = 7.95$ ,  $\text{p}K_{\text{enH}^+} = 10.79$ ) determined previously<sup>5</sup> under the same conditions as those employed in the present work. The results concerning  $\text{pH}$  measurements for  $\text{Zn}(\text{II})$  as the central cation in 1,2-ethanediamine solutions in the presence of

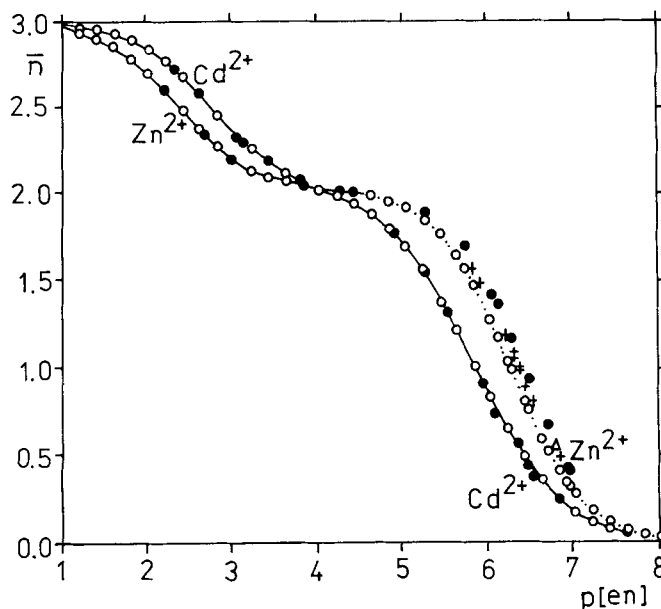


FIGURE 1 Formation curve ( $\bar{n}$  versus  $p[en]$ ) for the Zn(II) - en system in 3 M NaClO<sub>4</sub> at 25°. Experimental results with  $C_{Zn(ClO_4)_2} = 0.02$  M,  $C_{HClO_4} = 0.02$  M (●) and with  $C_{Zn(ClO_4)_2} = 0.1$  M,  $C_{HClO_4} = 0.1$  M (+) as well as with  $C_{Zn(ClO_4)_2} = 0.01$  M,  $C_{HClO_4} = 0.1$  M (Δ). The full and the dotted part of Zn(II) formation curve (○) is calculated with estimated chelate constants ( $\beta_{10} = 10^{6.50}$ ,  $\beta_{20} = 10^{12.46}$ ,  $\beta_{30} = 10^{14.82}$ , see text). For comparison the formation curve for the Cd(II) - en system in 3 M NaClO<sub>4</sub> at 25° is also given: (●) experimental points with  $C_{Cd(ClO_4)_2} = 0.02$  M,  $C_{HClO_4} = 0.02$  M and (○) calculated points with  $\beta_{10} = 10^{6.21}$ ,  $\beta_{20} = 10^{11.64}$ ,  $\beta_{30} = 10^{14.38}$  drawn on the basis of earlier measurements<sup>5</sup> are shown.

3 M NaClO<sub>4</sub> are presented in Fig. 1 where the cadmium formation curve is also shown for comparison. The studies performed showed that Zn(II) in 1,2-ethanediamine - 3 M NaClO<sub>4</sub> solutions at approximately neutral and weakly alkaline ranges is precipitated for values of  $\bar{n} < 1.9$  in the form of a white gelatinous solid. On the other hand, for  $\bar{n} > 1.9$  not a trace of hydroxo-complex was found to precipitate. It is worth noting that neither for Cd(II) under the conditions mentioned above nor in the Zn(II) - en - 1.2 M (K, H)NO<sub>3</sub> system were hydroxo-complexes found to precipitate<sup>2,5</sup> over the entire range of average ligand number. Thus, from pH measurements ( $C_{Zn(ClO_4)_2} = C_{HClO_4} = 0.02$  M) it was possible to determine only the third stepwise chelate stability constant, from the relationship provided by Bjerrum,<sup>2</sup> (1)

$$\log K_{30} = p[en] + \log (\bar{n} - 2)/(3 - \bar{n}) \quad (1)$$

from which the following value was calculated:

$$\log K_{30} = 2.36, \text{ for } p[en] = 2.657 \text{ and } \bar{n} = 2.333.$$

As will be shown later, the first two chelate constants may be obtained from measurements with the Zn(Hg) electrode at high 1,2-ethanediammonium diperchlorate concentrations (0.50 or 0.75 M). On the basis of the cumulative stability constants determined by this method ( $\beta_{10} = 10^{6.50}$ ,  $\beta_{20} = 10^{12.46}$ ) the value of  $\beta_{30}$  ( $= 10^{12.46} \times K_{30} = 10^{14.82}$ ) was calculated. For  $\bar{n} > 1.9$  the values of the average ligand number (○) calculated on the basis of the above chelate constants are in good

agreement with the experimental points (●) and this part of the zinc formation curve calculated was denoted by a full line, whereas for  $\bar{n} < 1.9$ , where a precipitate was found, the curve is shown as a dotted line (Figure 1).

*Chelated, non-chelated and partly-chelated complex formation*

As shown in Fig. 1, for  $\text{Zn}(\text{ClO}_4)_2$ , it was not possible to select conditions such that the contribution not only of protonated complexes but also of hydroxo-complexes would be negligible for the entire formation curve. Therefore, it was decided to determine a set of stability constants simultaneously for the chelate and protonated complexes coexisting in labile equilibrium at a large excess of the ligand salt, on the basis of the total complexation function (2)

$$F_{\text{ooo}} = \frac{C_{\text{Zn}(\text{ClO}_4)_2}}{[\text{Zn}^{2+}]} = 1 + \sum_{i=1}^{N} \sum_{j=1}^{M} \sum_{k=1}^{K} \beta_{ijk} [\text{en}]^i [\text{enH}^+]^j [\text{OH}^-]^k \quad (2)$$

where  $\beta_{ijk} = \frac{[\text{Zn}(\text{en})_i(\text{enH})_j(\text{OH})_k]^{(2+j-k)}}{[\text{Zn}^{2+}][\text{en}]^i[\text{enH}^+]^j[\text{OH}^-]^k}$  is the cumulative stability constant

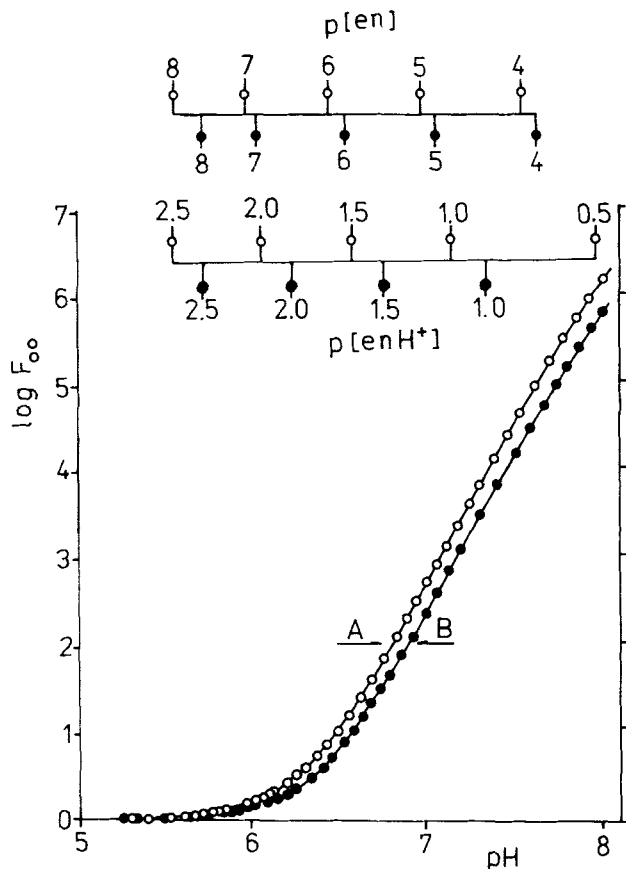


FIGURE 2 Logarithm of total complexation function ( $\log F_{\text{ooo}}$ ) plotted as a function of pH. Experimental results are with  $C_{\text{Zn}(\text{ClO}_4)_2} = 0.00479 \text{ M}$ ,  $C_{\text{enH}_2(\text{ClO}_4)_2} = 0.75 \text{ M}$ ,  $C_{\text{NaClO}_4} = 1.49 \text{ M}$  for curve A (○) and  $C_{\text{Zn}(\text{ClO}_4)_2} = 0.00479 \text{ M}$ ,  $C_{\text{enH}_2(\text{ClO}_4)_2} = 0.50 \text{ M}$ ,  $C_{\text{NaClO}_4} = 1.99 \text{ M}$  for curve B (●). The abscissa also shows the corresponding values of  $p[\text{en}]$  and  $p[\text{enH}^+]$ .

TABLE I

Results of glass- and Zn(Hg)-electrode measurements in 3 M (Na,H)ClO<sub>4</sub> with C<sub>Zn(ClO<sub>4</sub>)<sub>2</sub></sub> = 0.00479 M, C<sub>enH<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub></sub> = 0.75 M, C<sub>NaClO<sub>4</sub></sub> = 3 - 2C<sub>enH<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub></sub> - 2C<sub>Zn(ClO<sub>4</sub>)<sub>2</sub></sub>, pK<sub>enH<sub>2</sub><sup>2+</sup></sub> = 7.93, pK<sub>enH<sup>+</sup></sub> = 10.81<sup>a</sup>. Data is given for 11 of the 42 solutions studied.

No	pH	p[en]	p[enH <sup>+</sup> ]	F <sub>ooo</sub>	(E <sub>exp</sub> - E <sub>calc</sub> ) <sup>b</sup>
1	5.291	8.281	2.762	1.020	-0.19 mV
5	5.660	7.545	2.395	1.131	-0.07
9	5.841	7.184	2.215	1.293	0.02
13	6.094	6.684	1.968	1.948	0.05
17	6.306	6.267	1.763	3.952	-0.03
21	6.550	5.791	1.531	15.36	0.00
25	6.829	5.256	1.275	122.95	0.01
29	7.058	4.829	1.077	806.7	0.01
33	7.308	4.382	0.880	65.04 × 10 <sup>2</sup>	-0.06
37	7.631	3.845	0.666	88.48 × 10 <sup>3</sup>	0.07
41	7.941	3.384	0.515	86.23 × 10 <sup>4</sup>	-0.03

<sup>a</sup>Ref. 5. <sup>b</sup>Calculated with: log β<sub>10</sub> = 6.49, log β<sub>20</sub> = 12.44, log β<sub>30</sub> = 14.88, log β<sub>01</sub> = 1.03, log β<sub>11</sub> = 7.47, log β<sub>21</sub> = 12.81.

for the Zn(en)<sub>i</sub>(enH)<sub>j</sub>(OH)<sub>k</sub><sup>(2+j-k)</sup> complex. Calculations were carried out with acid dissociation constants of the 1,2-ethane-diammonium cation (pK<sub>enH<sub>2</sub><sup>2+</sup></sub> = 7.93, pK<sub>enH</sub> = 10.81) determined previously<sup>5</sup> under the same conditions.

The results of the studies for the two main measurement series A) C<sub>Zn(ClO<sub>4</sub>)<sub>2</sub></sub> = 0.00479 M, C<sub>enH<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub></sub> = 0.75 M, C<sub>NaClO<sub>4</sub></sub> = 1.49 M, and B) C<sub>Zn(ClO<sub>4</sub>)<sub>2</sub></sub> = 0.00479 M, C<sub>enH<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub></sub> = 0.50 M, C<sub>NaClO<sub>4</sub></sub> = 1.99 M, are presented in Fig. 2. A representative part of the experimental data is listed in Table I. Experimental data from each titration were the basis of least-squares calculations. The function minimized was

$$S = \sum_{i=1}^{i=N} w_{(F_{ooo})_i} ((F_{ooo}^{\text{exper.}})_i - (F_{ooo}^{\text{calc.}})_i)^2 \quad (3)$$

where N is the number of experimental points and  $w_{(F_{ooo})_i} = 1/(F_{ooo})_i^2$  is the weight of i-th data point.

The results of computer calculations are summarized in Table II. The best solution,

TABLE II  
Results of calculations of stability constants for the Zn(en)<sub>i</sub>(enH)<sub>j</sub><sup>(2+j)+</sup> complexes.

log(β <sub>ij</sub> ± σ <sub>ij</sub> )	I	II	III	IV	V
log(β <sub>00</sub> ± σ <sub>00</sub> ) (β <sub>00</sub> = 1.0)	(β <sub>00</sub> = 1.0)	(β <sub>00</sub> = 1.0)	-0.0006 ± 0.004	(β <sub>00</sub> = 1.0)	(β <sub>00</sub> = 1.0)
log(β <sub>10</sub> ± σ <sub>10</sub> )	6.56 ± 0.01	6.59 ± 0.004	6.56 ± 0.01	6.56 ± 0.007	6.49 ± 0.02
log(β <sub>20</sub> ± σ <sub>20</sub> )	12.53 ± 0.005	12.46 ± 0.005	12.48 ± 0.005	12.48 ± 0.004	12.44 ± 0.01
log(β <sub>30</sub> ± σ <sub>30</sub> )	15.64 ± 0.025	14.95 ± 0.11	15.09 ± 0.06	15.09 ± 0.06	14.88 ± 0.12
log(β <sub>01</sub> ± σ <sub>01</sub> )			0.83 ± 0.17	0.81 ± 0.07	1.03 ± 0.06
log(β <sub>11</sub> ± σ <sub>11</sub> )					7.47 ± 0.13
log(β <sub>21</sub> ± σ <sub>21</sub> )		12.77 ± 0.03	12.71 ± 0.03	12.71 ± 0.02	12.81 ± 0.03
S/f × 10 <sup>34</sup>	1.1652	0.1508	0.07992	0.07780	0.06176

<sup>a</sup>S is the sum of weighted squares of residuals, f is the number of degrees of freedom.

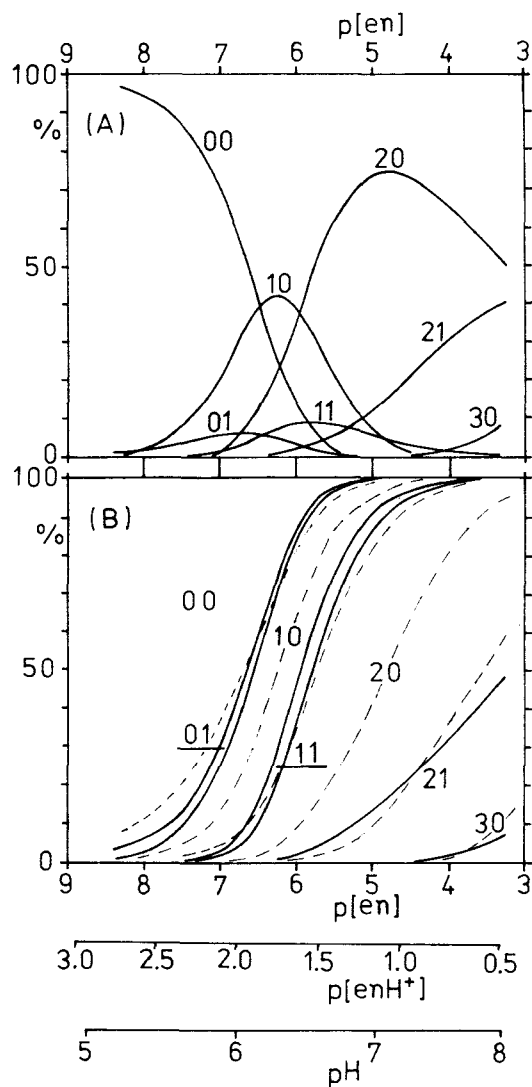
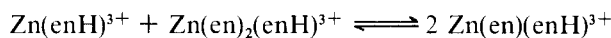


FIGURE 3 Distribution of Zn(II) among various complexes as a function of  $p[en]$  for  $C_{enH_2(ClO_4)_2} = 0.75$  M. The abscissa also shows the corresponding values of  $pH$  and  $p\ enH^+$ . Figure A: 10 =  $Zn(en)^{2+}$ ; 20 =  $Zn(en)_2^{2+}$ ; 30 =  $Zn(en)_3^{2+}$ ; 01 =  $Zn(enH)^{3+}$ ; 11 =  $Zn(en)(enH)^{3+}$ ; 21 =  $Zn(en)_2(enH)^{3+}$ , calculated for model V. Figure B, full line: Zn(II) complexes, dashed line: Cd(II) complexes (calculated with  $\beta_{10} = 10^{6.21}$ ,  $\beta_{20} = 10^{11.64}$ ,  $\beta_{30} = 10^{14.38}$ ,  $\beta_{01} = 10^{1.70}$ ,  $\beta_{11} = 10^{7.88}$ ,  $\beta_{21} = 10^{12.23}$ ).

$(S/f) \times 10^3 = 0.06176$ , was obtained by assuming that there are six complexes coexisting in the solution (Model V). Under these conditions the maximum contribution from the part chelate  $Zn(en)(enH)^{3+}$  complex is 9.15% (Fig. 3). For this reason its consideration in calculations is evident in the values of the reduced sum of weighted squares of residuals (0.0778 without allowance, 0.06176 with allowance for  $Zn(en)(enH)^{3+}$ ). On the other hand, according to the Bjerrum's theory of reversible step reactions, there are no obstacles whatsoever for coexistence of the  $Zn(en)(enH)^{3+}$  complex if only the  $Zn(enH)^{3+}$  and  $Zn(en)_2(enH)^{3+}$  complexes are present. The existence of the

Zn(en)(enH)<sup>3+</sup> complex results from the following reaction



as indicated by the equilibrium constant value,  $K = \beta_{11}^2/\beta_{01}\beta_{21} = 10^{1.1}$ . However, evaluation of the stability constant for the part-chelate Zn(en)(enH)<sup>3+</sup> complex, which is formed in the predominance region of the tetrahedral chelate complex, is possible only at sufficiently high 2-aminoethylammonium cation concentrations ( $C_{\text{enH}_2(\text{ClO}_4)_2} > 0.50 \text{ M}$ ).

During the study, no complexes containing more than one 2-aminoethylammonium cation or hydroxo-complexes were found to be formed. Finally, it was estimated how high the chelate stability constants of Zn(II)-1,2-ethanediamine complexes in perchlorate media (2.98 M NaClO<sub>4</sub> + 0.2 M HClO<sub>4</sub>) should be if no hydroxo-complexes would precipitate (see Table III). From a knowledge of the chelate constants for the Cd(II) and Zn(II) en complexes in 1.2 M (K, H)NO<sub>3</sub> (from Ref. 2) and the chelate constants for Cd(II) en complexes in 3 M (Na, H)ClO<sub>4</sub> (from Ref. 5) it was possible to estimate the chelate constants for the Zn(II) en complexes in 3 M (Na, H)ClO<sub>4</sub>. A comparison between the values of stepwise stability constants (columns d-f in Table III) indicated that the value of  $\log(K_{30} \pm \sigma_{30}) = 2.44 \pm 0.12$  obtained from the measurements is in acceptable agreement with the experimental value of  $\log K_{30} = 2.36$  derived from the formation function and its estimation (2.52). On the other hand, a comparison between obtained and estimated values of stepwise stability constants for Zn(en)<sup>2+</sup> and Zn(en)<sub>2</sub><sup>2+</sup> shows a very good agreement (Table III).

One may conclude therefore, that the cumulative stability constants for model V of Table II are a good approximation for calculations of the equilibrium concentrations of Zn(en)<sub>i</sub>(enH)<sub>j</sub><sup>(2+i)+</sup> complexes coexisting in labile equilibrium in sodium perchlorate solutions (Fig. 3). However, standard deviations for the Zn(en)<sub>3</sub><sup>3+</sup> and Zn(en)(enH)<sup>3+</sup> complex cations are relatively high.

An attempt was also made to calculate  $\beta_{02}$  and  $\beta_{12}$  but these constants could not be determined directly from the experimental data. However, the formation of the Zn(enH)<sub>2</sub><sup>4+</sup> complex at a very low concentration may be expected from the reaction  $2 \text{Zn(en)(enH)}^{3+} \rightleftharpoons \text{Zn(en)}_2^{2+} + \text{Zn(enH)}_2^{4+}$ . A comparison of the results ( $\log K_{01} = 1.03$ ,  $\log K_{11} = 0.98$ ) summarized in Table III leads to a conclusion that the value of the stepwise stability constant for Zn(enH)<sub>2</sub><sup>4+</sup> should be close to both values given above ( $K_{02} \approx 10$ ).

As indicated in Table IV, the first stepwise Zn(II) ammonia complex is about 24 times more stable than the first Zn(II) 2-aminoethylammonium complex. The zinc(II) ion

TABLE III  
Comparison of Cd(II) and Zn(II) ethanediamine stepwise stability constants in KNO<sub>3</sub> and NaClO<sub>4</sub>.

log K <sub>ij</sub>	Cd(II)	Zn(II)	Cd(H)	Zn(H)	Zn(II)	Zn(II)
log K <sub>10</sub>	5.63 <sup>a</sup>	5.92 <sup>a</sup>	6.21 <sup>b</sup>	6.49 <sup>d</sup>	6.50 <sup>c</sup>	
log K <sub>20</sub>	4.59 <sup>a</sup>	5.15 <sup>a</sup>	5.43 <sup>b</sup>	5.95 <sup>d</sup>	5.99 <sup>c</sup>	
log K <sub>30</sub>	2.07 <sup>a</sup>	1.85 <sup>a</sup>	2.74 <sup>b</sup>	2.44 <sup>d</sup>	2.52 <sup>c</sup>	2.36 <sup>f</sup>
log K <sub>01</sub>			1.70 <sup>c</sup>	1.03 <sup>d</sup>		
log K <sub>11</sub>			1.67 <sup>c</sup>	0.98 <sup>d</sup>		
log K <sub>21</sub>			0.59 <sup>c</sup>	0.37 <sup>d</sup>		

<sup>a</sup>Experimental values, Bjerrum method,<sup>2</sup> 1.2 M (K, H)NO<sub>3</sub>. <sup>b</sup>Experimental values, Bjerrum method,<sup>5</sup> 3 M (Na, H)ClO<sub>4</sub>. <sup>c</sup>Experimental values, Cd(Hg) measurements,<sup>3</sup> 3 M (Na, H)ClO<sub>4</sub>. <sup>d</sup>Experimental values, Zn(Hg) measurements, 3 M (Na, H)ClO<sub>4</sub>, this work. <sup>e</sup>Estimated values:  $\log K_{10} = 6.21 + (5.92 - 5.63) = 6.50$ ,  $\log K_{20} = 5.43 + (5.15 - 4.59) = 5.99$ ,  $\log K_{30} = 2.74 + (1.85 - 2.07) = 2.52$ , on the basis of Bjerrum's measurements.<sup>2</sup> <sup>f</sup>Experimental values, Bjerrum method, 3 M (Na, H)ClO<sub>4</sub>, this work.



TABLE IV  
Comparison of Cd(II) and Zn(II) ethanediamine and ammonia stability constants.

Cd(II) <sup>a</sup> or Zn(II), en(enH <sup>+</sup> ) 3 M, 25°		Cd(II) or Zn(II), NH <sub>3</sub> , 2 M, 25° <sup>b</sup>		Found	
Cd(II), log β <sub>01</sub>	= 1.70	Cd(II), log K <sub>1</sub>	= 2.69	Cd(II), log (K <sub>1</sub> /β <sub>01</sub> )	= 0.99, <sup>a</sup>
Zn(II),	= 1.03	Zn(II),	= 2.41	Zn(II),	= 1.38
Cd(II), log β <sub>10</sub>	= 6.21	Cd(II), log K <sup>2</sup>	= 2.14		
Zn(II),	= 6.49	Zn(II),	= 2.48		
Cd(II), log β <sub>11</sub>	= 7.88	Cd(II), log K <sub>3</sub>	= 1.48	Cd(II), log(β <sub>11</sub> /β <sub>10</sub> )	= 1.67, <sup>a</sup>
Zn(II),	= 7.47	Zn(II),	= 2.54	Zn(II),	= 0.98
Cd(II), log β <sub>20</sub>	= 11.64	Cd(II), log K <sub>4</sub>	= 0.97		
Zn(II),	= 12.44	Zn(II),	= 2.19		
Cd(II), log β <sub>21</sub>	= 12.23	Cd(II), log K <sub>5</sub>	= -0.32	Cd(II), log(β <sub>21</sub> /β <sub>20</sub> )	= 0.59, <sup>a</sup>
Zn(II),	= 12.81	Zn(II),		Zn(II),	= 0.37
Cd(II), log β <sub>30</sub>	= 14.38	Cd(II), log K <sub>6</sub>	= -1.66		
Zn(II),	= 14.88	Zn(II),			

<sup>a</sup>Ref. 5, <sup>b</sup>Ref. 1.

forms a stronger bond with 1,2-ethanediamine than cadmium(II) does. In the case of the soft cadmium(II) ion the situation is quite the opposite. The Cd(II)-2-aminoethylammonium bond is stronger than the corresponding one formed with zinc(II). Chelate ring formation allows maximum coordination number. This effect is particularly evident for Zn(II) (Table IV). However, the Zn(II) ethanediamine complexes show a less pronounced tendency to achieve an octahedral configuration<sup>11</sup> than the cadmium complexes.<sup>12</sup> This is also confirmed by the log β<sub>21</sub>/β<sub>11</sub> ratio which is 0.37 and 0.59 for Zn(II) and Cd(II), respectively. Thus, as in the case of Cd(II) as the central cation,<sup>5</sup> the Zn(II) ethanediamine complexes change in configuration from tetrahedral to octahedral and proceed through the Zn(en)<sub>2</sub>(enH)<sup>3+</sup> complex. The chelation effects in the Zn(II)-1,2-ethanediamine system relative to ammonia system are higher than in the Cd(II) systems (see Table V). Therefore, the decrease of the stepwise stability constant for the Zn(enH)<sup>3+</sup> complex (K<sub>01</sub>) with the simultaneous increase of the stepwise stability constants for the Zn(en)<sub>2</sub><sup>2+</sup> complexes (K<sub>10</sub>), in comparison with the K<sub>01</sub> and K<sub>10</sub> values obtained for the Cd(II)-1,2-ethanediamine system, seem to be in good agreement with the differences in properties of both central cations (Cd<sup>2+</sup> and Zn<sup>2+</sup>) and ligands (en and enH<sup>+</sup>).

As shown in Fig. 3A, the maximum contribution from the Zn(enH)<sup>3+</sup> complex is 5.9%. Only at pH ≤ 5.3 is the concentration of Zn(enH)<sup>3+</sup> higher than that of Zn(en)<sup>2+</sup>. Figure 3B shows clearly that the deviation from pure chelation over the predomination

TABLE V  
Chelation effects in Zn(II) or Cd(II)-1,2-ethanediamine systems relative to ammonia (estimated according to Bjerrum's relationships<sup>13</sup>).

	Zn(II)	Cd(II)
log $\frac{\beta_{10}(\text{en})}{K_1(\text{NH}_3)}$	4.1	3.0 <sup>a</sup>
log $\frac{\beta_{20}(\text{en})}{\beta_2(\text{NH}_3)}$	7.5	6.5 <sup>a</sup>

<sup>a</sup>Ref. 5.

range of tetrahedral configuration is small. The concentration of  $\text{Zn(en)}_2(\text{enH})^{3+}$  is strongly influenced by the total ligand salt concentration. It decreases from 40% (for  $C_{\text{enH}_2(\text{ClO}_4)_2} = 0.75 \text{ M}$ ,  $\text{pH} = 8$ ) to 18% (for  $\text{pH} = 8$ ,  $C_{\text{enH}_2(\text{ClO}_4)_2} = 0.20 \text{ M}$ ). In a similar manner, the  $\text{Zn(en)(enH)}^{3+}$  concentration decreases rapidly with a decrease in total ligand salt concentration. For  $C_{\text{enH}_2(\text{ClO}_4)_2} = 0.20 \text{ M}$  and  $\text{pH} \leq 8$  chelation is so dominant that the maximum contributions of the  $\text{Zn(enH)}^{3+}$ ,  $\text{Zn(en)(enH)}^{3+}$  and  $\text{Zn(en)}_3^{2+}$  complexes are approximately equal (about 3%) and negligible.

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