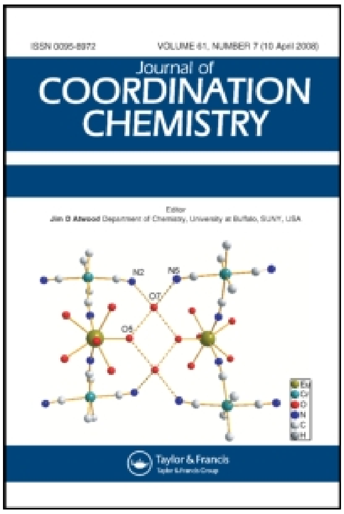

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THE EVALUATION OF STABILITY CONSTANTS OF PROTONATED ZINC-1,2-ETHANEDIAMINE COMPLEXES USING ISO-CONCENTRATION FUNCTIONS

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Complex formation between Zn(II) ion and 1,2-ethanediamine (en) or 2-aminoethylammonium cation (enH^+) has been re-examined in 3M (Na, H)ClO_4 at 25°, by measuring the e.m.f. of glass and Zn(Hg) electrodes. The iso-concentration functions procedure was applied to the determination of the cumulative stability constants of the $Zn(en)_i(enH)_j^{(2+j)+}$ complexes. The following values of cumulative stability constants were calculated from: (i) iso-p[en] functions, $\beta_{10} = 10^{6.488 \pm 0.008}$, $\beta_{01} = 10^{1.03 \pm 0.02}$, $\beta_{11} = 10^{7.43 \pm 0.14}$, $\beta_{20} = 10^{12.48 \pm 0.13}$; (ii) iso-p[$enH^+$] functions, $\beta_{10} = 10^{6.53 \pm 0.01}$, $\beta_{01} = 10^{1.01 \pm 0.03}$; (iii) iso-pH functions, $\beta_{10} = 10^{6.490 \pm 0.04}$, $\beta_{01} = 10^{1.03 \pm 0.01}$, $\beta_{11} = 10^{7.46 \pm 0.11}$, $\beta_{20} = 10^{12.46 \pm 0.11}$, by a least-squares computer method. The properties and applicabilities of the iso-concentration functions are also discussed.

INTRODUCTION

Zn(II) - 1,2-ethanediamine chelate complex formation has been studied by several authors.[1-16] In these studies the pH-metric Bjerrum method[1-11,17] or pH-metric Schwarzenbach approach,[12-15,18] potentiometric Leden method[4,19] and polarographic Lingane, De Ford and Hume procedure[4,16,20,21] were used. Complexation of Zn(II) with the monoprotonated form of 1,2-ethanediamine was reported recently.[22] Then the cumulative stability constants for the $Zn(en)_i(enH)_j^{(2+j)+}$ complexes were determined.[23,24] At present the solution of the function of several variables ($\overline{n}$ or F_{OO}) may be readily obtained using high-speed digital computers.[25] However, if weak non- and partly-chelated complexes as well as very stable chelated complexes coexist, some doubts may arise as to the correctness of the finally selected model of complexation equilibria. For instance, such doubts arise from the results, obtained recently by Shapnik *et al.*,[23] in 2M (Na,H)NO_3 solution, which differ considerably[†] from the stability constants determined previously both for the chelated[1-16] and protonated complexes.[24]

This paper presents the results obtained in a continuation of studies on the simultaneous complexation equilibria of Zn(II) cation with 1,2-ethanediamine or 2-aminoethylammonium cation in 3M (Na,H)ClO_4. Thus, it was possible to avoid complexation with the nitrate ion (at its high concentrations (*cf* Ref. 28) and low pH). Calculations were carried out by means of the Schwarzenbach and Szilárd iso-pH functions method.[29,30] By restricting studies to the pH range from 3 to 6.2 it was possible to rule out the complexation process with the hydroxyl ion (*cf* Ref. 31). As a supplement to the Schwarzenbach and Szilárd iso-pH

[†] Contrary to the perchlorate solutions,[24] in the nitrate medium[23] no precipitation of hydroxo-complexes (*cf* Ref. 1) was found to occur even at relatively high $Zn(NO_3)_2$ concentrations. Hence, the application of the Österberg method[26] (based upon the Bjerrum average ligand number[17] and determination of the non-complexed chelating ligand concentration according to the modified Hedström procedure[27]) was possible in the nitrate medium.

functions[29,30] two further iso-concentration functions (iso-p [en] and iso-p [enH^+])[32,33] were applied. Experimental verification of the above iso-concentration functions was the purpose of the present work. The properties of the iso-concentration functions as well as their applicability to studies of weak complexation with a monoprotonated form of a ligand in the presence of strong complexation with the chelating form of 1,2-ethanediamine are also discussed.

EXPERIMENTAL

Reagents and Apparatus

Glass electrodes (Radiometer G202C) or Kawai type amalgam electrodes[35] were used in combination with the Kawai's half-cell[36] (as a reference electrode) for e.m.f. measurements. Potentiometric titrations were performed by means of an Orion Digital Ionalyzer Research Model 701 A. Both the preparation of amalgam (about 1.5% by weight) and titrations were performed under argon. The titrant was delivered from calibrated Hamilton (10 or 100 μl) syringes. The temperature was maintained at 25 ± 0.1° by means of an ultrathermostat. All further titration equipment and the chemicals were the same as those described previously.[24]

The Method of Measurement

An appropriate set of total complexation functions (Eq. 1) was obtained by titration with 3M NaOH of the four solutions which contained $C_{Zn(ClO_4)_2}$ = 4.79 × 10^{-3} M) and $C_{enH_2(ClO_4)_2}$ = 1.00 M, 0.75 M, 0.625 M or 0.50 M). All solutions also contained $NaClO_4$ in the concentration $C_{NaClO_4} = 3.0 - 2C_{enH_2(ClO_4)_2} - 2C_{Zn(ClO_4)_2}$, so that the total concentration of all ions was constant The values of the total complexation function were calculated on the basis of e.m.f. measurements with the Zn(Hg) electrode using Eq. *1*,

$$F_{oo} = \frac{C_{Zn(ClO_4)_2}}{[Zn^{2+}]} = 10^{(E_s - E_{c_i})/29.58} \tag{1}$$

where E_s (= $E^\circ + E_j + 29.58 \log C_{Zn(ClO_4)_2}/a_{Zn(Hg)} + 29.58 \log f_i$) is the Zn(Hg) electrode potential over the range of pH (= 3 - 4.8), p[en] (= 12 - 9), p[enH^+] (= 5 - 3) in which no complexation with en and enH^+ takes place. E_{c_i} (= $E^\circ + E_j + 29.58 \log[Zn^{2+}]/a_{Zn(Hg)} + 29.58 \log f_i$) is the Zn(Hg electrode potential over the range of pH (> 4.8) in which complex formation could be detected.

The values of E_s over the mentioned pH range were constant and reproducible to within 0.2 mV. It was thus assumed that: (i) the activity coefficient, $f_{Zn(II)}$, is constant while the liquid junction potential caused by migration of Zn(II) through the phase boundary (sample/3M $NaClO_4$ salt bridge) is negligible (low and constant $C_{Zn(ClO_4)_2}$) and (ii) the effect of H^+, enH^+ and enH^{2+} concentration changes on the liquid junction potential may also be considered negligible since substitution of 1M $NaClO_4$ with 1M (1/2 enH_2^{2+} + enH^+) has practically no influence on the values of $pK_{enH_2^{2+}}$ (7.95, 7.93) and pK_{enH^+} (10.79, 10.81).[34] Thus, as a reasonable approximation, changes in E_j may be neglected and the activity coefficients of all positive ions, f_i, may be assumed to be constant. Finally, it is permissible to assume, within the experimental error, that these changes in medium have no influence on the stability constants of the Zn(II) complexes.

pH (= $-\log[H^+]$) was determined by glass electrode measurements as mentioned in our previus paper.[34] Equilibrium concentrations of complexing 1,2-ethanediamine forms were determined with acid dissociation constants of the 1,2-ethanediammonium cation ($pK_{enH^{2+}_2} = 7.93$, $pK_{enH^+} = 10.81$) determined previously under the same conditions.[34] Disturbances in the acid-base equilibria, resulting from the introduction of Zn(II) into ligand solutions ($C_{Zn(ClO_4)_2} \ll C_{enH_2(ClO_4)_2}$) have been considered to be negligible. This is because under these conditions the equilibrum concentrations of the 2-aminoethylammonium cation were in labile equilibrium with the high equilibrium concentrations of the 1,2-ethanediammonium cation (buffer solution).

RESULTS

Evaluation of Stability Constants Using Iso-Concentration Functions

It is notable that even at high $Zn(ClO_4)_2$ concentrations (0.02 or 0.10 M) the formation function does not depend on total Zn(II) concentration.[24] Thus, under the present conditions of large ligand salt excess, it may be assumed that the total complexation function (Eq. *1, 2*)

$$F_{oo}([en],[enH^+]) = 1 + \sum_{i=1}^{i=N} \sum_{j=1}^{j=M} \beta_{ij}[en]^i[enH^+]^j \qquad (2)$$

is the function of two variables ([en], [enH$^+$]). Hence, on the basis of measurements (Eq. *1, 2*) three different sets of iso-concentration functions may be obtained by interpolation.[32,33] Only a short summary is given here. The graphical procedure of iso-concentration functions is discussed more completely in Ref. 33. A set of four total complexation functions illustrating the procedure is shown in Figure 1.

(i) Iso-p[L] Functions of Total Complexation

At a constant equilibrium concentration of the chelating ligand, [en] = const., and at variable equilibrium concentration of the monodentate ligand, [enH$^+$], the iso-chelate function of total complexation is obtained as follows in (*3*) to (*6*)

$$F_{oo}([en],[enH^+])_{[en]} = F_o([en])_{[en]} + \sum_{j=1}^{j=M} \beta_j^{en}[enH^+]^j \qquad (3)$$

where

$$F_o([en]) = 1 + \sum_{i=1}^{i=N} \beta_{io}[en]^i \qquad (4)$$

$$\beta_1^{en} = \beta_{01} + \beta_{11}[en] + \beta_{21}[en]^2 \qquad (5)$$

$$\beta_2^{en} = \beta_{02} + \beta_{12}[en] + \beta_{22}[en]^2, etc. \qquad (6)$$

F_o ([en]) is pure chelate complexation; β_j^{en} are apparent stability constants.

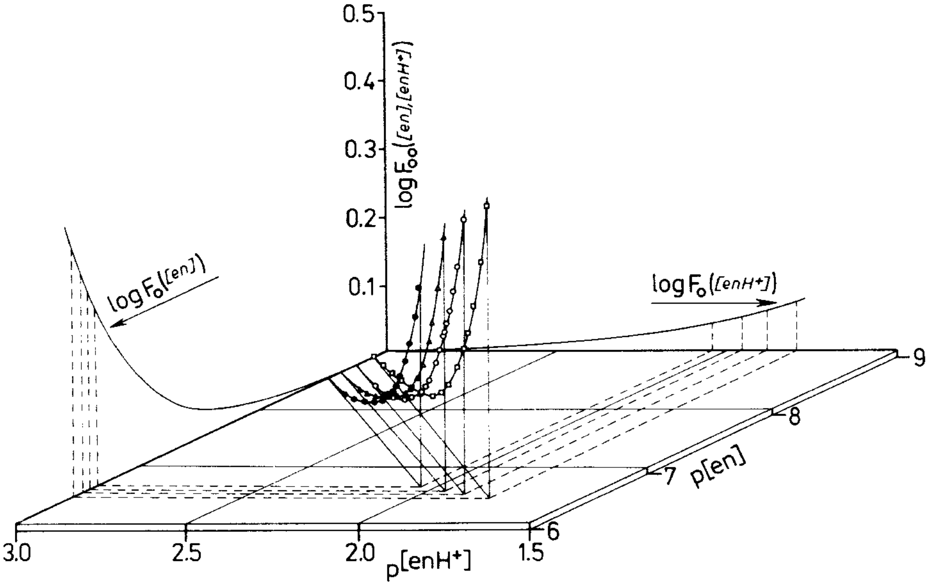

FIGURE 1 Logarithm of total complexation function (log F_{oo}) plotted as a function of negative logarithm of equilibrium 2-aminoethylammonium concentration (p[enH$^+$]) and of negative logarithm of equilibrium 1,2-ethanediamine concentration (p[en]). Experimental points with $C_{enH_2(ClO_4)_2}$ = 1.0 M(□), 0.75 M (○), 0.625 M (△), 0.50 M (●), $C_{Zn(ClO_4)_2} = 4.79 \times 10^{-3}$ M, $C_{NaClO_4} = 3.0 - 2C_{enH_2(ClO_4)_2} - 2C_{Zn(ClO_4)_2}$. For comparison, the logarithm of chelate complexation function ($\log F_o([en]) = \log(1 + \beta_{10}[en] + \beta_{20}[en]^2)$) calculated with $\beta_{10} = 10^{6.49}$, $\beta_{20} = 10^{12.46}$ and the logarithm of non-chelate complexation function ($\log F_o([enH^+]) = \log(1 + \beta_{01}[enH^+])$) calculated with $\beta_{01} = 10^{1.03}$ are also shown.

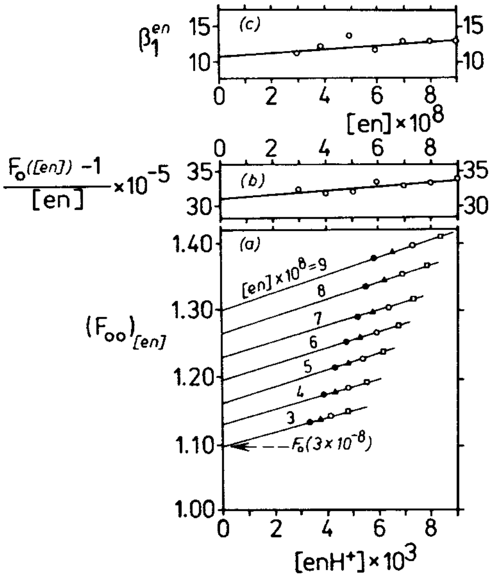

FIGURE 2 Iso-chelate functions. Evaluation of chelate complexation ($F_o([en])$) and apparent stability constant (β_1^{en}) for [en] = 3×10^{-8}, 4×10^{-8}, . . . , 9×10^{-8} M (Figure 2a). Evaluation of cumulative stability constants (β_{10} and β_{20}) for chelated complexes (Figure 2b). Evaluation of cumulative stability constants (β_{01} and β_{11}) for protonated complexes (Figure 2c).

The rectilinear dependence of iso-concentration functions on monoprotonated ligand concentration indiates that apart from chelate complexes, the protonated complexes also coexist over the ligand concentratin range under investigation (Figure 2a). It follows from Eq. *3* that the dependence of total complexation yields the values of pure chelate complexation (Eq. *4*) on the function axis (Figure 2a). From the slopes of the iso-chelate functions (Figure 2a) the values of the apparent stability constant, β_{1i}^{en}, for seven 1,2-ethanediamine concentrations, are estimated. Using a Leden - type approach for solving Eq. *4*, the values of cumulative stability constants for chelated complexes are estimated (*Fig. 2b*). Finally, the following values are evaluated: $\beta_{10} = (30.75 \pm 0.75) \times 10^5$, $\beta_{20} |= (3.06 \pm 0.90) \times 10^{12}$, by a least-squares computer method. In a similar manner, from the dependence of the apparent stability constat (β_{1i}^{en}) versus equilibrium 1,2-ethanediamine concentration (Fig. 2c) the following cumulative stability constants are estimated: $\beta_{01} = 10.75 \pm 0.58$, $\beta_{11} = (2.69 \pm 0.89) \times 10^7$.

(ii) Iso-p[LH$^+$] functions of total complexation

At a constant equilibrium concentration of the monoprotonated ligand, [enH$^+$], and variable equilibrium concentration of the chelating ligand, [en], one can derive the iso-(non-chelate) function of total complexation (Eq. *7*)

$$F_{oo}([en],[enH^+])_{[enH^+]} = F_o([enH^+])_{[enH^+]} + \beta_1^{enH}[en] + \beta_2^{enH}[en]^2 + \beta_{30}[en]^3 \qquad (7)$$

where

$$F_o([enH^+]) = 1 + \beta_{01}[enH^+] + \beta_{02}[enH^+]^2 + \ldots \qquad (8)$$

$$\beta_1^{enH} = \beta_{10} + \beta_{11}[enH^+] + \beta_{12}[enH^+]^2 + \ldots \qquad (9)$$

$$\beta_2^{enH} = \beta_{20} + \beta_{21}[enH^+] + \beta_{22}[enH^+]^2 \qquad (10)$$

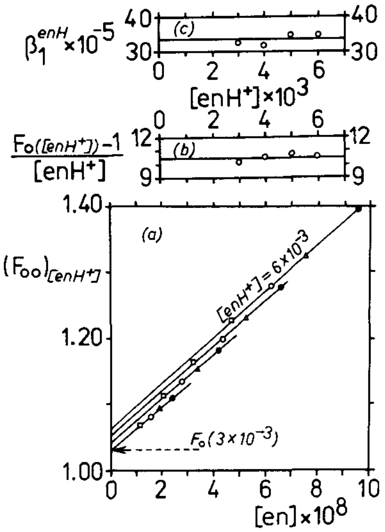

FIGURE 3 Iso(non-chelate) functions. Evaluation of non-chelate complexation ($F_0([enH^+])$) and apparent stability constant (β_{1i}^{enH}) for $[enH^+] = 3\times10^{-3}, 4\times10^{-3}, 5\times10^{-3}, 6\times10^{-3}$ M (Figure 3a). Evaluation of cumulative stability constant (β_{01}) for non-chelated complex (Figure 3b). Evaluation of cumulative stability constant (β_{10}) for first chelated complex (Figure 3c).

$F_0([enH^+])$ is a pure non-chelate complexation function; β_1^{enH} and β_2^{enH} are apparent stability constants. From iso-(non-chelate) functions of total complexation (Eq. *7*), first, the values of pure non-chelate complexation (Eq. *8*) are obtained at various values of $[enH^+] = 3 \times 10^{-3}, \ldots, 6 \times 10^{-3}$ M (Figure 3a). Since $(F_0([enH^+]) - 1)/[enH^+]$ against $[enH^+]$ is a straight line parallel to the abscissa (Figure 3b), it may be assumed that $Zn(enH)^{3+}$ is the only non-chelate complex over the lignad concentration range under investigation. On the other hand, since the iso-(non-chelate) functions are straight lines (Figure 3a) and the first apparent stability constant, β_1^{enH}, does not depend on equilibrium concentration of the monoprotonated ligand (Figure 3c), it may be assumed that $Zn(en)^{2+}$ is the only chelated complex occuring at measurable concentration. Finally, it may be admitted that the concentrations of partly-chelated complexes are negligible under the conditions of investigation. The following values of the cumulative stability constants were obtained numerically: $\beta_{01} = 10.30 \pm 0.80$, $\beta_{10} = (33.69 \pm 1.07) \times 10^5$.

(iii) Iso-pH functions of total complexation

At a constant equilibrium concentration of the hydrogen ion and variable equilibrium concentration of the chelating ligand, *i.e.* at constant $[enH^+]/[en]$ ratio, the iso-pH function of total complexation is obtained as follows shown in (*11*) to (*15*)

$$F_{oo}([en],[enH^+])_{[H^+]} = 1 + \sum_{j=1}^{j=M} \beta_j^{pH} [en]^j \qquad (11)$$

where

$$\beta_1^{pH} = \beta_{10} + \beta_{01} k_1^H [H^+] \qquad (12)$$

$$\beta_2^{pH} = \beta_{20} + \beta_{11} k_1^H [H^+] + \beta_{02}(k_1^H [H^+])^2 \qquad (13)$$

$$\beta_3^{pH} = \beta_{30} + \beta_{21} k_1^H [H^+] + \beta_{12}(k_1^H [H^+])^2 + \beta_{03}(k_1^H [H^+])^3 \qquad (14)$$

$$\beta_4^{pH} = \beta_{22}(k_1^H [H^+])^2 + \beta_{13}(k_1^H [H^+])^3 + \beta_{04}(k_1^H [H^+])^4 \qquad (15)$$

TABLE I

The iso-pH functions; corresponding values of $[H^+]$, $[en]$, $F_{oo}([en], [enH^+])_{[H^+]}$ in 3M (Na,H)ClO$_4$ with $C_{Zn(ClO_4)_2} = 0.00479$ M, $C_{enH_2(ClO_4)_2} = 1.0, 0.75, 0.625, 0.50$ M, $C_{NaClO_4} = 3 - 2C_{enH_2(ClO_4)_2} - 2C_{Zn(ClO_4)_2}$, $pK_{enH_2^{2+}} = 7.93$, $pK_{enH^+} = 10.81$ from Ref. 34.

	$C_{enH_2(ClO_4)_2}$							
	1.0 M (□)		0.75 M (○)		0.625 (△)		0.50 M (●)	
$[H^+] \times 10^6$	$[en] \times 10^8$	$(F_{oo})_{[H^+]}$	$[en] \times 10^8$	$(F_{oo})_{[H^+]}$	$[en] \times 10^8$	$(F_{oo})_{[H^+]}$	$[en] \times 10^8$	$(F_{oo})_{[H^+]}$
2.0	4.58	1.219	3.38	1.159	2.86	1.134	2.30	1.106
1.9	5.07	1.240	3.77	1.175	3.17	1.146	2.54	1.116
1.8	5.64	1.263	4.21	1.194	3.53	1.160	2.795	1.1265
1.7	6.29	1.291	4.73	1.215	3.95	1.178	3.12	1.139
1.6	7.04	1.325	5.29	1.239	4.42	1.196	3.54	1.156
1.5	8.16	1.375	6.00	1.268	5.01	1.221	4.06	1.177
1.4	9.32	1.426	6.98	1.310	5.74	1.252	4.60	1.198
1.3	10.74	1.492	8.36	1.370	6.71	1.292	5.18	1.221
1.2	12.60	1.576	9.80	1.433	7.96	1.343	5.78	1.245
1.1	14.90	1.684	11.20	1.495	9.36	1.403	7.55	1.319
1.0	18.28	1.845	13.55	1.600	11.32	1.487	9.036	1.380

where

β_j^{pH} are the apparent stability constants[18,29,30] and $k_1^H = (1/K_{enH^+} = 10^{10.81})$ is the protonation constant determined previously.[34] Rearrangement of Eq. *11* leads to the first successive iso-pH function (*16*)

$$(F_{10})_{[H^+]} = (((F_{oo})_{[H^+]} - 1)/[en])_{[H^+]} = \sum_{j=1}^{j=M} \beta_j^{pH}[en]^{(j-1)} \qquad (16)$$

from which the values of β_j^{pH} are determined successively at various values of $[H^+]$ according to the Schwarzenbach and Szilárd method.[29,30]

A representative part of the data is listed in Table I. In Figure 4a $(F_{10})_{[H^+]}$ is plotted as a function of [en] at eleven constant values of $[H^+]$. Straight lines were obtained which indicate that the value of M is 2 (see Eq. *11*, *16*). From these straight lines the values of β_1^{pH} and β_2^{pH} were determined (Figure 4a). The rectilinear dependence of these apparent stability constants versus $[H^+]$ indicates that the complexes $Zn(enH)^{3+}$, $Zn(en^{2+}$, $Zn(en)(enH)^{3+}$ and $Zn(en)_2^{2+}$ coexist over the $[H^+]$ range under investigation. Final values of cumulative stability constants were estimated numerically as follows: $\beta_{10} = (30.92 \pm 0.28) \times 10^5$, $\beta_{01}^H = (6.92 \pm 0.18) \times 10^{11}$, $\beta_{01} = 10.71 \pm 0.28$, $\beta_{20} = (2.87 \pm 0.72) \times 10^{12}$, $\beta_{11}^H = (1.84 \pm 0.47) \times 10^{18}$, $\beta_{11} = (2.86 \pm 0.73) \times 10^7$

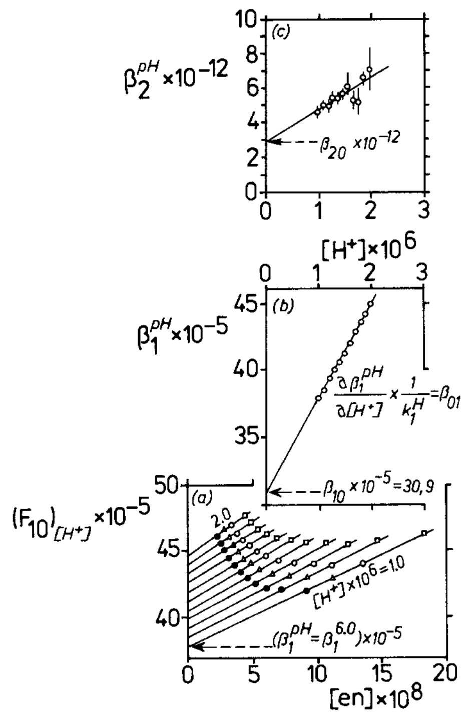

FIGURE 4 Iso-pH functions. Evaluation of apparent stability constants (β_1^{pH} and β_2^{pH}) from first successive iso-pH function ($(F_{10})_{[H^+]}$) for $[H^+] = 1.0 \times 10^{-6}$, 1.1×10^{-6}, . . . , 2×10^{-6} M (Figure 4a). Evaluation of cumulative stability constant (β_{10}) for first chelated complex and of cumulative stability constant (β_{01}^H or β_{01}, see Eq. 18) for non-chelated complex (Figure 4b). Evaluation of cumulative stability constant (β_{20}) for second chelated complex and of cumulative stability constant (β_{11}^H or β_{11}) for partly-chelated complex (Figure 4c).

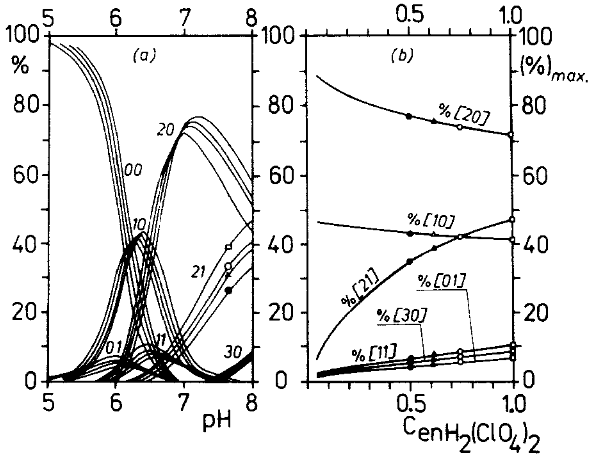

FIGURE 5 Distribution of Zn(II) among various complexes as a function of pH for the series with $C_{enH_2(ClO_4)_2} = 1.0$ M (□), 0.75 M (○), 0.625 M (△), 0.50 M (●): Figure 5a. Maximum contribution of $Zn(en)_i(enH)_j^{(2+j)+}$ complexes as a function of total $enH_2(ClO_4)_2$ concentration (Figure 5b). The curves are calculated with $\beta_{01} = 10^{1.03}$, $\beta_{10} = 10^{6.49}$, $\beta_{11} = 10^{7.46}$, $\beta_{20} = 10^{12.46}$ (present measurements) and with $\beta_{21} = 10^{12.81}$, $\beta_{30} = 10^{14.88}$ (from Ref. 24).

where

$$\beta_{ij}^{H} = [Zn(en)_i(enH)_j^{(2+j)+}]/[Zn^{2+}][en]^{(i+j)}[H^+]^j \qquad (17)$$

$$\beta_{ij} = \beta_{ij}^{H}/(k_1^H)^j \qquad (18)$$

The distribution of Zn(II) among various complexes for particular measuring series is shown in Figure 5a. The dependence of the maximum contribution of a particular complex versus total 1,2-ethanediamine diperchlorate concentration is illustrated in Figure 5b. The calculations included also the complexes formed at 8 ⩾ pH > 6, $Zn(en)_2(enH)^{3+}$ and $Zn(en)_3^{2+}$, whose stability constants were determined previously.[24]

DISCUSSION

If only the properties of the central cation would allow this, it would be desirable to determine the set of stability constants by stages: first, for chelated complexes by the Bjerrum method[1,17] and then for non- and partly-chelated complexes by the Leden method.[19] Such a procedure might be applied to studies of Cd(II) complexation with ethanediamine.[34] However, for the Zn(II) - en - 3M(Na,H)ClO$_4$ system the formation function method[1,17] or such a related method as the so-called "metal-ion excess curve" and "metal-ion equivalent curve" procedure described by Schwarzenbach[18] as well as the "iso-pH formation functions" approach reported by Österberg[26] could not have been used for determination of β_{10} and β_{20} constants. This is because on one hand ($C_{Zn(ClO_4)_2} \gtrsim C_{enH_2(ClO_4)_2}$) hydroxo-complexes are being precipitated, and on the other hand ($C_{Zn(ClO_4)_2} \ll C_{enH_2(ClO_4)_2}$) the values of $\bar{n}$ (or g-values[18]) become inaccurate, particularly at low pH values. In the latter case one should apply the Leden total complexation function obtained from potentiometric measurements of central cation concentration.[19] Then the stability constants may be achieved by a trial and error method, using the weighted least-squares curve-fitting algorithm.[25] At last, the final model of complexation equilibria is selected by verifying particular hypotheses by means of an F-test.[37] Such a procedure was applied in our previous paper.[24] At present, a more systematic method which requires no preliminary assumptions[29,30] was used. The Schwarzenbach and Szilárd iso-pH functions were expressed here in terms of equilibrium ligands concentrations (Eq. *11* and *16*) instead of total ligand salt concentration (*cf* Ref. 30, p. 1227). This made possible introduction of two further iso-concentration functions (iso-p[L] and iso-p[LH]). These functions can be considered as an extension of the Schaap and McMasters method described previously for classical ternary systems.[38]

As shown in Figure 2 and 4, from the iso-p[en] and iso-pH functions it was possible to estimate the stability constants for two protonated complexes, $Zn(enH)^{3+}$ and $Zn(en)(enH)^{3+}$, and two chelated complexes, $Zn(en)^{2+}$ and $Zn(en)_2^{2+}$. On the other hand, from the iso-p[enH^+] functions the stability constants were estimated for two complexes only, $Zn(enH)^{3+}$ and $Zn(en)^{2+}$. This apparent inconsistency results from the properties of iso-concentration functions. The maximum value of the iso-p[enH^+] function is limited not by the maximum ligand salt concentration but by its minimum value ($C_{enH_2(ClO_4)_2} = 0.50$ M, Figure 3a). Under these conditions the concentrations of $Zn(en)(enH)^{3+}$ and $Zn(en)_2^{2+}$ are about 1.2% and 1.8% of the iso-p[enH^+] function of total complexation, respectively. Hence, the stability constants β_{11} and β_{20} could not have been estimated. On the other hand, under the conditions of iso-p[en] or iso-pH functions the concentrations of $Zn(en)(enH)^{3+}$ and $Zn(en)_2^{2+}$ are sufficient (about 4% and 5%, respectively) to estimate the stability constants β_{11} and β_{20}. A good agreement between the stability constants determined now (over the pH range from 4.8 to 6.2) and those obtained in the previous paper[24] indicates that the assumption of neglecting the complexation with the hydroxyl ion also for $6 < pH \leqslant 8$ was justified (Table III). However, the stability constants obtained now differ considerably from those obtained by Shapnik *et al.*[23] These authors, in the most important range of average ligand numbers for graphical determination, $\bar{n} \lesssim 0.6$, report only two iso-pH formation functions (for pH = 6.1 and 6.3). The absence of a sufficient number of iso-pH functions in that range of $\bar{n}$, makes graphical solution impossible by the method of successive extrapolations. Also by a numerical method†, for the data provided by Shapnik *et al.*[23] it was not possible to determine reliable stability constants (for some pH values negative values of apparent stability constants were obtained).

On the basis of existing determinations one can find out that the stability constant for $Zn(enH)^{3+}$ should be lower not only than the corresponding constant for the $Ag(enH)^{2+}$ complex (Table II) but also than the value of β_{01} for the Cd(II) complex with 3-aminopropylammonium cation ($10^{1.86}$ Ref. 30, $10^{1.83}$ Ref. 39). On the other hand, the analysis of the apparent stability constants in particular iso-concentration functions (for Zn(II)- or Cd(II)- - - $NaClO_4$ system) leads to conclusion that it is not possible to determine β_{01} and β_{11} from measurements at $C_{enH_2(ClO_4)_2} \approx C_M$ when $\beta_{10}/\beta_{01} > 10^{4.2}$. Under these conditions the average ligand numbers theoretically calculated by the Bjerrum[17] and Österberg[26] methods are practically equal since the values of non-complexed 1,2-ethanediamine concentrations estimated according to the Bjerrum relationship[17] or, by the modified Hedström equation[27,40-43] are very close to each other. For instance, for $C_{Zn(ClO_4)_2} = 0.05$ M, the only protonated complex which should be taken into account in calculations is $Zn(en)_2(enH)^{3+}$. Its concentration is 5.7%, for pH = 8.0 (Figure 5b). Since this complex is formed over a considerable predominance

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† For Cu(II) - (O-phosphorylethanolamine)- system, very close values, $\beta_{01} = 10^{1.85 \pm 0.02}$, $\beta_{10} = 10^{6.38 \pm 0.03}$, $\beta_{11} = 10^{8.18 \pm 0.03}$, $\beta_{20} = 10^{12.40 \pm 0.03}$, to stability constants graphically found by Österberg,[26] were obtained.

TABLE II

Summary of the cumulative stability constants for metal-ion complexes with 1,2-ethanediamine and N-methyl-substituted 1,2-ethanediamine; en: 1,2-ethanediamine; men: *N*-Methyl-1,2-ethanediamine; trimen: *N,N,N'*-Tris-methyl-1,2-ethanediamine; tetramen: *N,N,N',N'*-Tetramethyl-1,2-ethanediamine.

L	M	$M(LH)_j$		$M(L)_i(LH)_j$			$M(L)_i$			Ref.
		log β_{01}	log β_{02}	log β_{11}	log β_{12}	log β_{21}	log β_{10}	log β_{20}	log β_{30}	
en	Ag^{+}	2.35^{a} ±0.05					4.7^{a} ±0.1	7.7^{a} ±0.1		a:46
en	Ag^{+}	2.42^{b} ±0.17	$(5.12)^{b}$				5.06^{b} ±0.06	$(7.66)^{b}$		b:47
en	Ag^{+}	2.91^{c1} ±0.02	6.07^{c1} ±0.02				6.13^{c1} ±).02			c1:48
en	Ag^{+}	2.79^{c2}	6.0^{c2}	8.12^{c2}			5.26^{c2}	$(9.45)^{c2}$		c2:49,50
en	Ag^{+}	2.34^{c3} ±0.02	4.90^{c3} ±0.02	6.47^{c3} ±0.02				7.64^{c3} ±0.02		c3:51
en	Hg^{2+}		12.9^{d} ±0.1	18.6^{d} ±1.0	22.3^{d} ±0.3		14.3^{d} ±0.1	22.3^{d} ±0.1		d:52
en	Hg^{2+}	7.8^{e}	14.2^{e}				14.3^{e}	23.4^{e}		e:53
en	Cd^{2+}	1.5^{f}	2.8^{f}				5.63^{g}	10.22^{g}	12.29^{g}	f:54 g:1
en	Cd^{2+}	1.70^{h} ±0.03		7.88^{h} ±0.03		12.230^{h} ±0.005	6.21^{i}	11.64^{i}	14.38^{i}	h:34 i:34
en	Zn^{2pl}	1.03^{j1} ±0.06		7.47^{j1} ±0.13		12.81^{j1} ±0.03	6.49^{j1} ±0.01	12.44^{j1} ±0.01	14.88^{j1} ±0.12	j1:24
en	Zn^{2+}	1.03^{j2} ±0.02		7.43^{j2} ±0.14			6.488^{j2} ±0.008	12.48^{j2} ±0.13		this work
en	Znf^{2+}	1.01^{j3} ±0.03					6.53^{j3} ±0.01			this work
en	Zn^{2+}	1.03^{j4} ±0.01		7.46^{j4} ±0.11			6.490^{j4} ±0.004	12.46^{j4} ±0.11		this work
en	Zn^{2+}	1.86^{k1} ±0.26		8.59^{k1} ±0.35			6.25^{k1} ±0.23	12.31^{k1} ±0.39		k1:23
en	ZN^{2+}	2.72^{k2} ±0.15	5.86^{k2} ±0.39	9.15^{k2} ±0.27	12.15^{k2} ±0.25	13.13^{k2} ±0.46	6.23^{k2} ±0.28	10.00^{k2} ±0.30	13.35^{k2} ±0.40	k2:23
en	Cu^{2+}	4.30^{l}	8.31^{l}	14.54^{l}			9.95^{l}	20.94^{l}		l:55
men	Cd^{2+}	1.486^{m} ±0.139					5.474^{m} ±0.004	9.563^{m} ±0.015	11.396^{m} ±0.129	m:45
trimen	Cd^{2+}	0.825^{m} ±0.042					4.560^{m} ±0.004	6.731^{m} ±0.015		m:45
tetramen	Cd^{2+}	1.041^{m} ±0.02					3.869^{m} ±0.004	5.168^{m} ±0.039		m:45

[a]Glass electrode, 20°, 0.1($NaNO_3$). [b]Glass electrode, 25°, 1.0(KNO_3). [(c1–c2)]Glass electrode, 25°, 3($LiClO_4$); $pK_w = 14.22$ for 3($NaClO_4$)[c1] from Ref. 56; $pK_w = 13.867 \pm 0.009$ for 3($LiClO_4$)[c2]. [c3]Glass, silver-ion selective electrode, 25°, 0.5(KNO_3). [d]Glass, mercury electrode, polarography, 25°, 0.1(KNO_3). [e]Glass, mercury electrode, 25°, 1.3(KNO_3). [f]Polarography, 25°, 1.2($enH_2(ClO_4)_2$). [g]Glass electrode, 25°, 1.2(KNO_3). [h]Glass, Cd(Hg) electrode, 25°, 3($NaClO_4$). [i]Glass electrode, 25°, 3($NaClO_4$). [(j1–j4)]Glass, Zn(Hg electrode, 25°, 3($NaClO_4$): Leden's method[j1]; (iso-p[L])[j2]; (iso-p[LH^+])[j3]; iso-pH functions[j4]. [(k1–k2)]Glass electrode, 20°, 2($NaNO_3$); Osterberg's method, graphical[k1], numerical[k2] constants. [m]Glass, cadmium-ion selective electrode, 25°, 1(KNO_3).

range of the tetrahedral $Zn(en)_2^{2+}$ complex[44] (90%) it is usually neglected in calculations (*cf* Figure 5b). This conclusion is confirmed by the results reported by Creyf and van Poucke[45] who for similar systems, determined β_{01} for $Cd(menH)^{3+}$, $\beta_{10}/\beta_{01} = 10^{3.99}$, and did not find any protonated complex in the Cd(II) - en - KNO_3 system (Table II).

In addition, it should be pointed out that the iso-chelate functions may be used over the entire pH range for determination of stability constants of complexes formed in solutions of both bi- and multidentate ligands.

Iso-(non-chelate) functions have not such a general significance. In bidentate ligand solutions, for $pH < \log(k_1^H k_{12}^H)^{1/2}$, a set of iso-(non-chelate) functions is obtained. It is essential that from these functions pure non-chelate complexation, $F_0([enH^+])$, may be estimated by means of the first extrapolation. On the other hand, for $pH > \log(k_1^H k_{12}^H)^{1/2}$, the iso-(non-chelate) functions merge together forming one monotonically increasing total complexation function which may only be solved numerically.[†]

Apart from the iso-pH formation functions introduced by Österberg,[26] the iso-p[L] and iso-p[LH] formation functions may also be obtained from the experimental data by interpolation.

The above mentioned iso-concentration functions exhaust the possibilities for graphical determination of the stability constants and each of them render a possible numerical solution without any *a priori* assumptions as to the composition or abundance of complexes formed in bidentate ligand solutions. In view of the fact that the iso-chelate, iso-(non-chelate) and iso-pH functions of total complexation are in different ways sensitive to the predominance of particular complexes, this approach appears to be more extensive for both determination and verification of particular stability constants obtained.

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[†] For multidentate ligands the iso-(non-chelate) functions are of auxiliary significance since they may be used only over that pH range where the complexation with only two ligand forms (*e.g.*, LH and L) is so predominant that complexation with other ligand forms may be neglected.

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