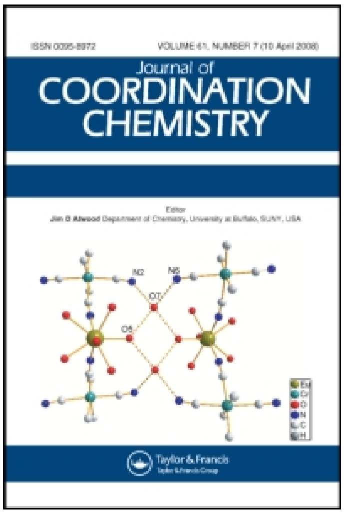

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THE EVALUATION OF STABILITY CONSTANTS OF PROTONATED MERCURY 1,2-ETHANEDIAMINE COMPLEXES USING ISO-CONCENTRATION FUNCTIONS

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A detailed study of complex formation between Hg(II) and 1,2-ethanediamine (en) and 2-aminoethylammonium cation (enH^+) has been performed with high initial 1,2-ethanediammonium diperchlorate concentrations ($C_{enH_2(ClO_4)_2} = 0.3333$ M, 0.25 M, 0.15 M or 0.05 M) and low initial Hg(II) concentration ($C_{Hg(ClO_4)_2} = 9.51 \times 10^{-4}$ M) in 3 M (Na, H)ClO_4 at 25°C, by measuring the e.m.f. of glass and mercury electrodes. The data for each constant level of p[en], p[enH^+] and pH were treated separately by an iso-concentration function of complexation procedure or by a generalized weighted least-squares computer method. The values for the cumulative stability constants of the following complexes were evaluated: $Hg(en)^{2+}$, $\beta_{10} = 10^{16.749 \pm 0.006}$; $Hg(enH)^{3+}$, $\beta_{01} = 10^{8.82 \pm 0.02}$; $Hg(en)(enH)^{3+}$, $\beta_{11} = 10^{20.751 \pm 0.007}$; $Hg(en)_2^{2+}$, $\beta_{20} = 10^{25.970 \pm 0.003}$.

Keywords: Mercury, ethylenediamine, stability constants, protonation, iso-concentration functions

INTRODUCTION

Hg(II)–1,2 ethanediamine chelate complex formation has been studied as early as in 1944 by Jannik Bjerrum.[1,2] On the basis of e.m.f. measurements with a mercury electrode Bjerrum[1] reported the value 11.71 for the logarithm of the mean complexity constant. In 1964 Bjerrum and Larsen[2] re-examined the $Hg(NO_3)_2$–en–1.3 M (K^+, H^+, Ba^{2+}), NO_3^- system and determined in two stages the stability constants for the chelated and the protonated non-chelated complexes. In the first stage the β_{20} value (for $Hg(en)_2^{2+}$) was determined from measurements with mercury and glass electrodes at relatively high concentrations ($C_{Hg^{2+}} > 0.02$–01 M, $C_{en} > 0.05$–0.5 M) and pH (6.8–10.45). In the second stage from potentiometric measurements at low concentrations ($C_{Hg^{2+}} = 2 \times 10^{-3} + 3.6 \times 10^{-5}$ M, $C_{en} = 0.05 - 3.7 \times 10^{-4}$ M) and pH (5.47–6.31), the complexation function ($C_{Hg^{2+}}/[Hg^{2+}] = X$) was calculated. Following the theory of reversible step reactions,[3] from a complexation function the contribution deriving from the $Hg(en)_2^{2+}$ complex was extracted and from the obtained set of linear equations ($X - \beta_{20}[en]^2$) the stability constants were calculated for the other complexes ($Hg(en)^{2+}$, $Hg(enH)_2^{4+}$ and $Hg(enH)^{3+}$) (Table I). In the meantime Nyman, Roe and Masson[4,5] have shown polarographically that the $Hg(en)_2^{2+}$ chelated complex is reversibly electroreduced at the dropping mercury electrode and have estimated its stability constant (for $C_{en} = 0.02$–1 M, pH = 11–12, 0.1 M KNO_3) by the De Ford and Hume method[6] (Table I). The existence of $Hg(en)_3^{2+}$ (for $C_{en} > 1$ M). and moreover the species $Hg(en)_4^{2+}$ (for $C_{en} > 2$M) is problematical, as those authors report.[4] Independently of Nyman *et al.*[4], Watters and Mason[7] have also found that mercury(II)—ethanediamine complexes are reversibly reduced at the DME (in alkaline solutions containing 0.004% of gelatin and 0.1 M KNO_3). From potentiometric measurements with the mercury electrode (for $C_{Hg^{2+}} = 10^{-2} - 10^{-4}$ M, $C_{en} = 5 \times 10^{-3} - 5 \times 10^{-2}$ M, $C_{NaClO_4} = 0.1$ M, pH = 3 – 9) Watters and Mason[7] have determined the stability constants for the complexes $Hg(en)^{2+}$, $Hg(enH)_2^{4+}$, $Hg(en)(enH)^{3+}$, $Hg(en)(OH)^{+}$, $Hg(en)_2^{2+}$, $Hg(en)(enH)_2^{4+}$ (by determinats using Cramer's rule, according to Sullivan and Hindman[8]).

As shown in Table I, reasonable agreement between the values of stability constants[1–2,4–5,7] is found only in the cases of the *mono*- and *bis*-(ethanediamine) chelate complexes, mainly due to experimental difficulties encountered in determining the much smaller stability constants for protonated non- and partly-chelated complexes.

This paper presents potentiometric results obtained in a continuation of studies on the simultaneous complexation equilibria of the zinc family cations[9–11] with 1,2-ethanediamine or 2-aminoethylammonium cation in 3 M $(Na,H)ClO_4$. On the basis of measurements with the mercury and glass electrodes (pH =3–7) at high total concentrations of 1,2-ethanediammonium diperchlorate (0.3333–0.05 M) with respect to total mercuric perchlorate ($\sim 10^{-3}$ M) the cumulative stability constants for $Hg(en)^{2+}$, $Hg(en)_2^{2+}$, $Hg(enH)^{3+}$ and $Hg(en)(enH)^{3+}$ have been determined using iso-concentration function procedures or direct computer methods.

EXPERIMENTAL

Reagents and Apparatus

Mercury(II) perchlorate solution was prepared by dissolving a weighed amount of mercury(II) oxide (Merck p.a.) in a known excess of $HClO_4$ (G.R. Merck) followed by dilution in boiled, triply-distilled water.[12] As a check, the Hg(II) concentration was determined either electrogravimetrically or by titration (with SCN^-, using Fe^{3+} as indicator, or by titration of standard NaCl solution with the $Hg(ClO_4)_2$ solution in question, using diphenylcarbazone as indicator[13]). The amount of $HClO_4$ in the mercury(II) perchlorate solution was determined by titration with standard NaOH solution after addition of KI (according to Qvarfort and Sillen[14]). Mercury (A.R. PoCh, Gliwice) was purified and redistilled just before use. 1,2-ethanediammonium diperchlorate, sodium perchlorate and sodium hydroxide were prepared and analysed as described previously.[10]

Glass electrodes (Radiometer G202C) or Kawai-type J-shape mercury electrodes[15] were used in combination with Kawai's reference half cell[16] for e.m.f. measurements. Potentiometric titrations were performed (under argon) by means of an Orion Digital Ionalyser Research Model 701A. The titrant was delivered from calibrated Hamilton syringes. Polarographic measurements were performed by means of a Radelkis OH–105 polarograph and a Laboratorni Pristroje Polarographic Analyser (PA-2 or PA-3).

The temperature was maintained at 25 ± 0.1°C by means of an ultra-thermostat. All further titration or polarographic equipment and chemicals used have been described previously.[10,17]

Method of Measurement

The main set of experimental data was obtained by titration with 3 M NaOH of solutions in which $C_{Hg(ClO_4)_2} = 9.5057 \times 10^{-4}$ M and $C_{enH_2(ClO_4)_2}$ =0.3333, 0.25, 0.15 or

TABLE I

Reported values of the cumulative stability constants for Hg(II) complexes with 1,2-ethanediamine.

$Hg(enH)^{(2+j)+}$		$Hg(en)_i(enH)_j^{(2+j)+}$		$Hg(en)_i^{2+}$			
log β_{01}	log β_{02}	log β_{11}	log β_{12}	log β_{10}	log β_{20}	log β_{30}	Ref.
					23.42[a]		1
					23.18[b]	23.06[b]	4
	12.9[c]	18.6[c]	22.3[c]	14.3[c]	23.3[c]		
	±0.1	±1	±0.3	±0.1	±0.1		6
					24.36[d1]	24.1[d1]	
					±0.04	±0.1	5
					23.18[d2]	23.09[d2]	
					±0.01	±0.02	5
					21.94[d3]	21.74[d3]	
					±0.01	±0.02	5
(7.8 ± 1)[e]	14.15[e]			14.34[e]	23.44[e]		
	±0.1			±0.1	±0.03		2
8.82[f]		20.751[f]		16.749[f]	25.970[f]		this work
±0.02		±0.007		±0.006	±0.003		

[a] Glass, mercury electrodes, 25°, 1(KNO_3); [b] Polarography, 25°, 0.1(KMO_3); [c] Glass, mercury electrodes, (polarography), 25°, 0.1($NaClO_4$) potentiometry, 0.1(KNO_3) polarography, $(Hg(en)(OH))^+$, log $\beta_{101} = 23.8 \pm 0.3$); [d1–d3] Polarography, 10° (d1), 25° (d2), 40° (d3), 0.1(KNO_3); [e] Glass, mercury electrodes, 25°, 1.3(KNO_3); [f] Glass, mercury electrodes, 25°, 3($NaClO_4$), the error limit given for log β_{ij} is $3\sigma(\log \beta_{ij})$.

0.05 M. All solutions also contained $NaClO_4 = 0.3333, 0.25, 0.15$ or 0.05 M. All solutions also contained $NaClO_4$ of concentrations $C_{NaClO_4} = 3 - 2C_{enH_2(ClO_4)_2} - 2C_{Hg(ClO_4)_2}$. In the absence of $enH_2(ClO_4)_2$ the Hg electrode potential in $C_{Hg(ClO_4)_2} = 9.5057 \times 10^{-4}$ M, $C_{NaClO_4} = 3.0$ M, $C_{HClO_4} = 10^{-3}$ M is given by (*1*)

$$E^{S}_{Hg} = E^{O1}_{Hg} + 29.58 \log(C_{Hg(ClO_4)_2}/K^{(pH=3)}) \qquad (1)$$

where

$$E^{O1}_{Hg} = {}^{EO}_{Hg} + E_j + 29.58 \log f_i, \text{ (c.f. Ref. 11).}$$

$$\begin{aligned} C_{Hg(ClO_4)_2} &= [Hg^{2+}]_s + [Hg_2^{2+}] + [Hg(OH)^+] + [Hg(OH)_2] + [Hg_2(OH)_2] \\ &\quad + [Hg_2(OH)^+] = [Hg^{2+}]_s K^{(pH=pH)} \end{aligned} \qquad (2)$$

For a given pH the $K^{(pH=pH)}$ value is expressed by (*3*)

$$K^{(pH=pH)} = 1 + 10^{2.63} + 10^{-3.55}/[H^+] + 10^{-6.21}/[H^+]^2 + 10^{-2.25}/[H^+]$$

after substitution of the appropriate equilibrium constants (*4*) to (*7*) into (*2*).

$$[Hg_2^{2+}] = K^{Hg}_o[Hg^{2+}] = 10^{2.63}[Hg^{2+}], \text{ (Ref. 12)} \qquad (4)$$

$$[Hg(OH)^+] = \beta^*_{1,1}[Hg^{2+}]/[H^+] = 10^{-3.55}[Hg^{2+}]/[H^+], \text{ (Ref. 18)} \qquad (5)$$

$$[Hg(OH)_2] = \beta^*_{1,2}[Hg^{2+}]/[H^+]^2 = 10^{-6.21}[Hg^{2+}]/[H^+]^2, \text{ (Ref. 18)}$$

$$\begin{aligned} [Hg_2(OH)^+] &= \beta^*_{1,1}[Hg_2^{2+}]/[H^+] = 10^{-4.88}[Hg_2^{2+}]/[H^+] \\ &= 10^{-2.25}[Hg^{2+}]/[H^+], \text{ (Ref. 19)} \end{aligned} \qquad (7)$$

Hence, for $C_{Hg(ClO_4)_2} = 9.5057 \times 10^{-4}$ M, $C_{NaClO_4} = 3$ M, $C_{HClO_4} = 10^{-3}$ M the constant $K^{(pH=3)}$ is 434.1 and the negative logarithm value of the equilibrium Hg(II) concentration ($p[Hg^{2+}]_s$) is equal to 5.6596.

The Hg electrode potential in the complexing medium ($C_{Hg(ClO_4)_2} = 9.5057 \times 10^{-4}$ M, $C_{enH_2(ClO_4)_2} = 0.3333 - 0.05$ M, $C_{NaClO_4} = 3 - 2C_{enH_2(ClO_4)_2} - 2C_{Hg(ClO_4)_2}$, $3 \leqslant pH \leqslant 7$) is given by (*8*)–(*9a*) and the

$$E^{c}_{Hg} = E^{o1}_{Hg} + 29.58 \log(C_{Hg(ClO_4)_2}/(K^{(pH=pH)} + (\Sigma/[Hg^{2+}]_c))) \qquad (8)$$

$$\begin{aligned} C_{Hg(ClO_4)_2} &= [Hg^{2+}]_c + [Hg_2^{2+}] + [Hg(OH)^+] + [Hg(OH)_2] + [Hg_2(OH)^+] + \sum \\ &= [Hg^{2+}]_c K^{(pH=pH)} + \sum, \end{aligned} \qquad (9)$$

$$\sum = \sum_h \sum_i \sum_j \sum_k [(Hg)_h(en)_i(enH)_j(OH)_k^{(2h+j-k)}], \qquad (9a)$$

$K^{(pH=pH)}$ value is given by (*3*). The equations (*1*) and (*8*) give the complexation function of the mercuric cation, F'_{oooo}, with the potential ligands (en, enH^+, OH^-), (*10*).

$$\begin{aligned} F'_{oooo} &= 10^{\left[\frac{E^s_{Hg} - E^c_{Hg}}{29.58} + \log K^{(pH=3)}\right]} - (K^{(pH=pH)} - 1) \\ &= \sum_h\sum_i\sum_j\sum_k [(Hg)_h(en)_i(enH)_j(OH)_k^{(2h+j-k)}] - (K^{(pH=pH)} - 1) \end{aligned} \qquad (10)$$

In the above equation the contribution deriving from $Hg(OH)_k^{2-k}$, $Hg_2(OH)^+$ and Hg_2^{2+} was subtracted.

To find out whether in the studied conditions polynuclear Hg(II) complexes would arise the E^c_{Hg} and pH measurements were performed for the following series: $C_{Hg(ClO_4)_2} = 4.75 \times 10^{-4}$ M or 3.17×10^{-4} M, $C_{enH_2(ClO_4)_2} = 0.3333$ M, $C_{NaClO_4} = 2.32$ M, and $C_{Hg(ClO_4)_2} = 1.90 \times 10^{-4}$ M, $C_{enH_2(ClO_4)_2} = 0.05$ M, $C_{NaClO_4} = 2.89$ M (and the E^s_{Hg} measurements for three above $Hg(ClO_4)_2$ concentrations in 3 M $NaClO_4$, pH = 3). The complexation functions calculated according to (*10*) for the above three series assume the curves $\log F'_{000} = f(pH)$ for $C_{Hg(ClO_4)_2} = 9.5057 \times 10^{-4}$ M, $C_{enH_2(ClO_4)_2} = 0.3333$ M or 0.05 M, respectively (Fig. 1). The average deviations were 0.16 mV, 0.20 mV or −0.25 mV, respectively (corresponding to the experimental error in the determination of $E^s_{Hg} - E^c_{Hg}$). It was thus assumed that at the concentrations studied only mononuclear Hg(II) complexes are present, and whose composition and cumulative stability constants could be determined from (*11*), the limiting form of (*10*)

$$F'_{000} = \sum_{i=O}^{i=N} \sum_{j=O}^{j=M} \sum_{k=O}^{k=K} \beta_{ijk} [en]^i [enH^+]^j [OH^-]^k \qquad (11)$$

where for i = j = O also k = K = O (contribution of the hydroxo-complexes subtracted, β_{ijk} is given by (*11a*)

$$\beta_{ijk} = \frac{[Hg(en)_i(enH)_j(OH)_k^{(2+j-k)}]}{[Hg^{2+}][en]^i[enH^+]^j[OH^-]^k} \qquad (11a)$$

For pH ⩾ 3 in (*10*) the $(K^{(pH=pH)} - 1)$ term could be replaced by $K^{(pH=pH)}$, since the maximum error of this simplification is 0.08% (for $C_{enH_2(ClO_4)_2} = 0.05$ M) and the error decreases with any increase of $C_{enH_2(ClO_4)_2}$ and pH. Moreover, for pH ⩾ 4.75 the term $(K^{(pH=pH)} - 1)$ could be neglected because at this pH value the error is only 0.125% and decreases with any $C_{enH_2(ClO_4)_2}$ and pH increase. In the $enH_2(ClO_4)_2$ medium the values of the equilibrium concentration of the non-complexed Hg(II) was determined from (*12*).

$$p[Hg^{2+}]_c = -\log[Hg^{2+}]_c = \frac{E^s_{Hg} - E^c_{Hg}}{29.58} + p[Hg^{2+}]_s \qquad (12)$$

Polarographic measurements confirmed that (*12*) could also be applied at high complexation of mercuric cation. The waves were reversible (for pH = 7–8), as indicated by the slope (31 mV) of the plot of the logarithmic wave analysis (performed according to Heyrovsky and Kuta[20]). $pH(= -\log[H^+])$ was determined by glass electrode measurements as mentioned in our previous paper.[9] Equilibrium concentrations of complexing 1,2-ethanediamine forms were determined with the protonation constants $k^H_1 = 10^{10.81}$, $k^H_{12} = 10^{7.93}$ determined previously under the same conditions.[9]

RESULTS AND DISCUSSION

Evaluation of Complex Compositions and Stability Constants Using Iso-concentration Functions

The results of the experimental studies with respect to (*11*) are presented in Fig. 1 together with the ranges of the negative logarithm of equilibrium concentrations of 2-aminoethylammonium cation or hydrogen ion as well as 1,2-ethanediamine for the

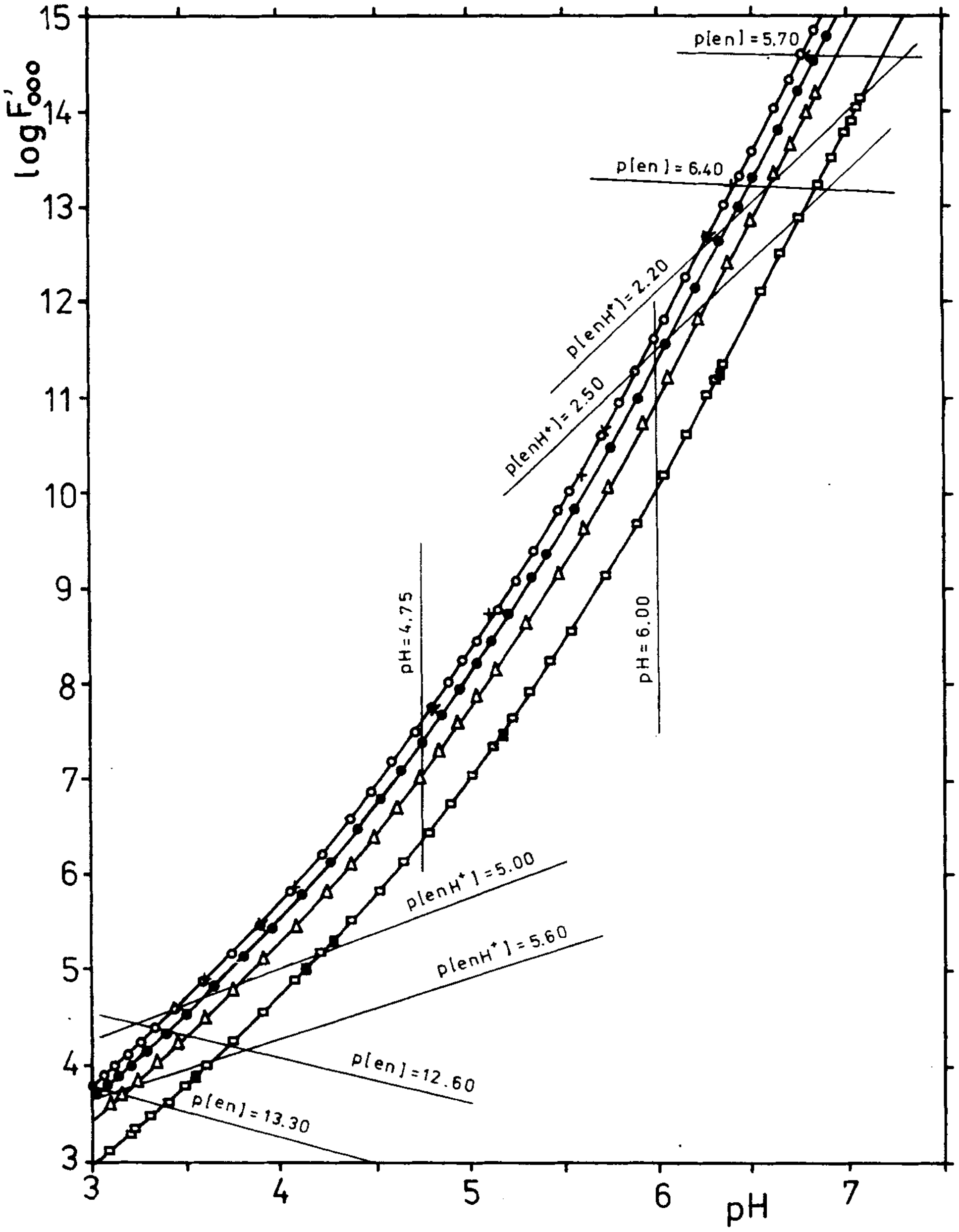

FIGURE 1 Logarithm of complexation function (log F'_{ooo}) plotted as a function of pH. Experimental points with $C_{Hg(ClO_4)_2} = 9.51 \times 10^{-4}$ M, $C_{enH_2(ClO_4)_2} = 0.3333$ M (○), 0.25 M (●), 0.15 M (△), 0.05 M (□), $C_{Hg(ClO_4)_2} = 4.75 \times 10^{-4}$ M, $C_{enH_2(ClO_4)_2} = 0.3333$ M (+), $C_{Hg(ClO_4)_2} = 3.17 \times 10^{-4}$ M, $C_{enH_2(ClO_4)_2} = 0.333$ M (×), $C_{Hg(ClO_4)_2} = 1.90 \times 10^{-4}$ M, $C_{enH_2(ClO_4)_2} = 0.05$ M (■), $C_{NaClO_4} = 3 - 2C_{enH_2(ClO_4)_2} - 2C_{Hg(ClO_4)_2}$. The ranges of the negative logarithm of equilibrium concentrations of 2-aminoethylammonium cation, hydrogen ion or 1,2-ethanediamine used in the next constructions (Figs 2–6) of the particular iso-concentration functions are also shown.

particular iso-concentration functions, next shown in Fig. 2–6, respectively. Experimental data from each titration were the basis of the weighted least-squares computer treatment. The basic relations for determination of stability constants with application of the iso-concentration functions are discussed in Refs. 11 and 21. Here only the relations for the very strong complexation potentially with the three ligands en, enH^+ and OH− will be given here.

(i) Iso-p[enH⁺] Functions

The partial derivative of the complexation function logarithm with respect to the logarithm of the equilibrium concentration of the chelate ligand (at constant equilibrium concentration of the monoprotonated ligand) gives the average ligand number with the chelate ligand (Eq. (*13*), Fig. 2a, b)

$$\bar{n}_{[\text{enH}^+]} = \left(\frac{\partial \log(F'_{ooo})}{\partial \log[\text{en}]}\right)_{[\text{enH}^+]} = \frac{\sum_{i=1}^{i=N} i\,\beta_i^{\text{enH}}[\text{en}]^i}{F_o([\text{enH}^+]) + \sum_{i=1}^{i=N} \beta_i^{\text{enH}}[\text{en}]^i}, \qquad (13)$$

where

$$F_o([\text{enH}^+]) = \sum_{j=0}^{M} \beta_{ojo}[\text{enH}^+]^j, \qquad (14)$$

$$\beta_1^{\text{enH}} = \sum_{k=0}^{k=2} \beta_{10k}[\text{OH}^-]^k + \sum_{j=1}^{j=(M-2)} \beta_{1jo}[\text{enH}^+]^j, \text{ and} \qquad (15)$$

$$\beta_2^{\text{enH}} = \sum_{k=0}^{k=2} \beta_{20k}[\text{OH}^-]^k + \sum_{j=1}^{j=2} \beta_{2jo}[\text{enH}^+]^j \qquad (16)$$

Not excluding *a priori* the possibility of existence of the octahedral complex we have $\beta_3^{\text{enH}} = \beta_{300}$ and $F'_{ooo} = F_o([\text{enH}^+]) + \sum_{i=1}^{i=N} \beta_i^{\text{enH}}[\text{en}]^i$, $N \leqslant 3$, $M \leqslant 2N$.

To establish the composition of complexes predominant over a given ligand concentration range, two partial derivatives $\bar{n}_{[\text{enH}^+]}$ (*13*) and $\bar{n}_{[\text{en}]}$ (*19*) should be examined at about the same concentration range.

At very high complexation (Fig. 2a), the mean $\bar{n}_{[\text{enH}^+]}$ values are 1.88 and 1.79 for $\text{p[enH}^+] = 2.20 = \text{const.}$, $\text{p[en]} = 6.80 - 5.93$ and $\text{p[enH}^+] = 2.50 = \text{const.}$, $\text{p[en]} = 7.40 - 6.56$, respectively. Since those values are close to $\bar{n}_{[\text{enH}^+]} = 2$ (see Fig. 2a), Hg(en)_2^{2+} could be regarded the highest chelate complex present over the examined concentration range. This conclusion was confirmed by the linear dependence of the $(G'_{200})_{[\text{enH}^+]}$ function on $([\text{en}])^{-1}$, given by Eq. (*17*) and shown in Fig. 3a.

$$(G'_{200})_{[\text{enH}^+]} = (F'_{ooo})_{[\text{enH}^+]}/[\text{en}]^2 = \beta_2^{\text{enH}} + \beta_1^{\text{enH}}([\text{en}))]^{-1}, \qquad (17)$$

valid for $(F'_{ooo})_{[\text{enH}^+]} \gg (F_o([\text{enH}^+]))_{[\text{enH}^+]}$.

The $(G'_{200})_{[\text{enH}^+]}$ data were treated separately for each constant level of $\text{p[enH}^+]$ by a least-squares computer procedure. The computed β_2^{enH} values, together with standard deviations are shown in Fig. 3b. Since the second apparent stability constant, β_2^{enH},

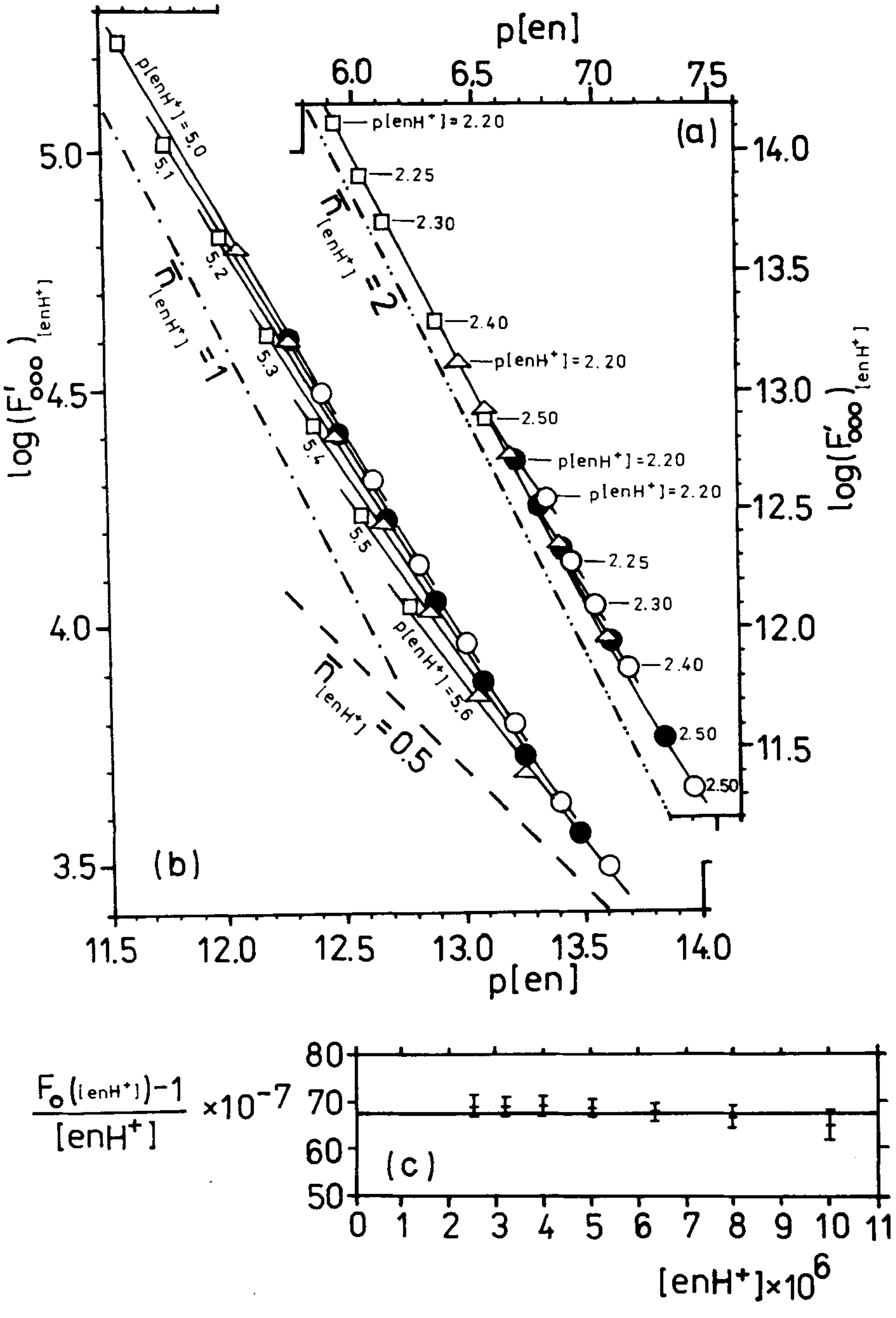

FIGURE 2 Iso-(non-chelate) functions at high (Fig. 2a) or low equilibrium 2-aminoethylammonium cation concentrations (Fig. 2b). For comparison, the average ligand numbers equal to 2 (–··–··–) 1 (–·–·–) or 0.5 (– – – –) are also shown. Evaluation of cumulative stability constant (β_{010}) for first non-chelate complex (Fig. 2c) is also shown.

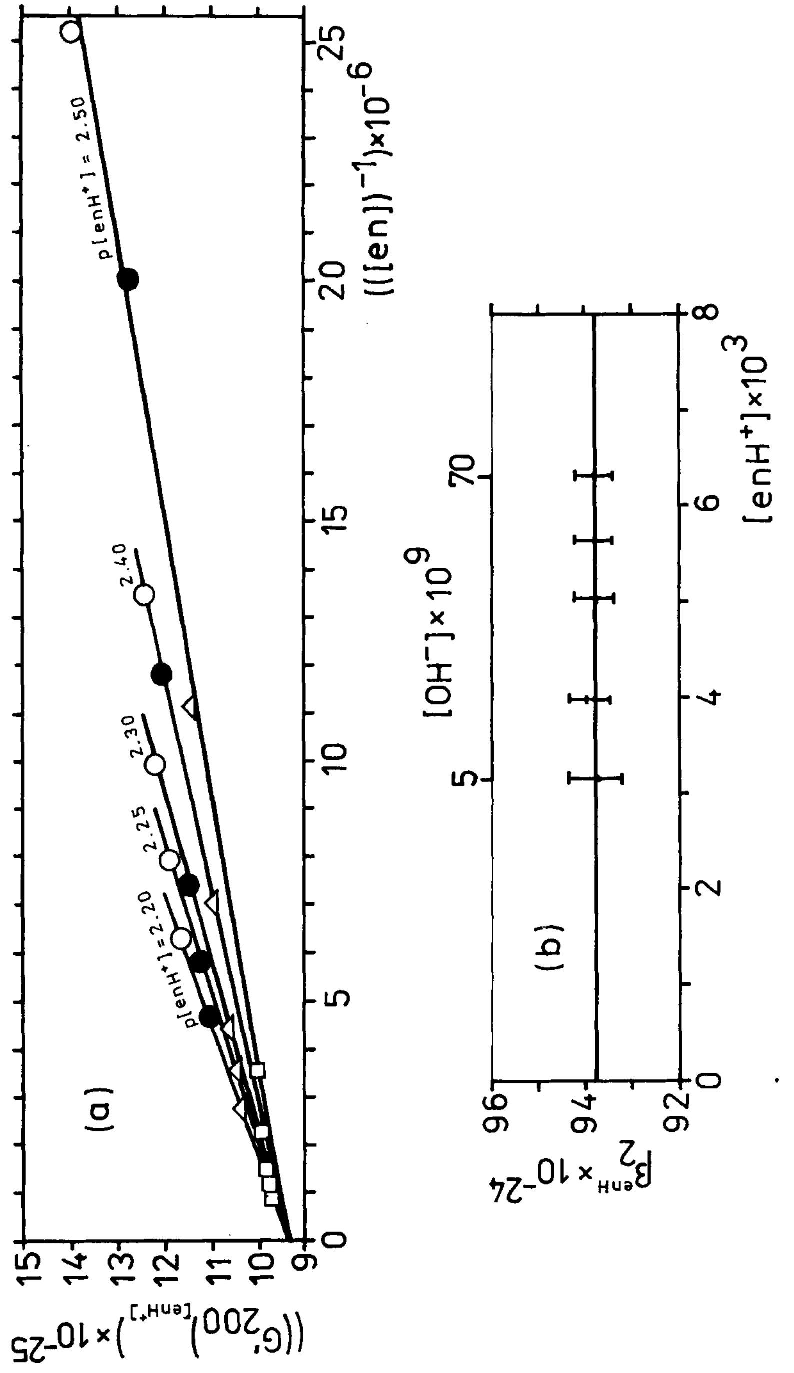

FIGURE 3 Iso-(non-chelate) functions; evaluation of apparent stability constant, β_2^{enH}, from $(G'_{200})_{[enH^+]} = f(([en])^{-1})$, (Eq. (17), Fig. 3a); evaluation of cumulative stability constant, β_{200}, for second chelated complex (Fig 3b).

does not depend on the equilibrium concentration of the monoprotonated ligand or on the equilibrium concentration of hydroxyl ion (Fig. 3b), it may be assumed that $Hg(en)_2^{2+}$ is the only chelated complex and that the concentrations of mixed (hydroxo-chelated) complexes are negligible over the high $[enH^+]$ range. Finally, the following value for the cumulative stability constant for $Hg(en)_2^{2+}$ was obtained numerically: $(\beta_{200} \pm \sigma_{200}) = (9.39 \pm 0.04) \times 10^{25}$, $\log(\beta_{200} \pm \sigma_{200}) = 25.973 \pm 0.002$.

On the other hand, at low values of the equilibrium concentration of the monoprotonated ligand ($p[enH^+] = 5.6 - 5.0$, Fig. 2b), the mean $\bar{n}_{[enH^+]}$ value changed from 0.61 to 0.86, for $p[enH^+] = 5.6 = \text{const.}$, $p[en] = 13.61 - 12.78$ and $p[enH^+] = 5.0 = \text{const.}$, $p[en] = 12.41 - 11.58$, respectively. Hence, in that ligand concentration range the coexistence of two complexes should be assumed: $Hg(en)^{2+}$ (predominant) and $Hg(enH)^{3+}$. We will demonstrate that our assumption is supported by analysis of $\bar{n}_{[en]}$ values.

From the dependence of iso-$p[enH^+]$ functions of complexation on equilibrium concentrations of chelated ligand (*18*),

$$(F'_{000})_{[enH^+]} = (F_0([enH^+]))_{[enH^+]} + \beta_1^{enH}[en] + \ldots \qquad (18)$$

the values of the non-chelate complexation function (*14*) and of the apparent stability constant (*15*) are obtained at various values of $[enH^+]$. Since $(F_0([enH^+]) - 1)/[enH^+])$ against $[enH^+]$ is a straight line parallel to the abscissa (Fig. 2c) it may be admitted that $Hg(enH)^{3+}$ is the only non-chelated complex occuring at measurable concentration under the investigated conditions. The following cumulative stability constant for $Hg(enH)^{3+}$ was estimated numerically:

$$(\beta_{010} \pm \sigma_{010}) = (6.77 \pm 0.21) \times 10^8, \ \log(\beta_{010} \pm \sigma_{010}) = 8.83 \pm 0.01.$$

(ii) Iso-p[en] Functions

The partial derivative of the complexation function logarithm with respect to the logarithm of the equilibrium monoprotonated ligand (at constant equilibrium concentration of chelated ligand) gives the average ligand number with monoprotonated ligand (*19*) Fig. 4a, b):

$$\bar{n}_{[en]} = \left(\frac{\partial \log(F'_{000})}{\partial \log[enH^+]}\right)_{[en]} = \frac{\sum_{j=1}^{j=M} j\beta_j^{en}[en]^j}{F_0([en]) + \sum_{j=1}^{j=M} \beta_j^{en}[en]^j} \qquad (19)$$

where

$$F_0([en)] = 1 + \sum_{i=1}^{i=2} \sum_{k=0}^{k=2} \beta_{i0k}[en]^i[OH^-]^k \qquad (20)$$

$$\beta_1^{en} = \sum_{i=0}^{i=2} \beta_{i10}[en]^i \qquad (21)$$

$$\beta_2^{en} = \sum_{i=0}^{i=2} \beta_{i20}[en]^i, \text{ etc.} \qquad (22)$$

At very high complexation (Fig. 4a) the mean $\bar{n}_{[en]}$ values are 0.04 and 0.09 for $p[en] = 5.7 = \text{const.}$, $p[enH^+] = 1.66 - 2.09$ and $p[en] = 6.4 = \text{const.}$, $p[enH^+] = 2.00 - 2.43$, respectively. Since in the approximately the same ligand concentration range the mean $\bar{n}_{[enH^+]}$ value was $1.9 - 1.8$ and hydroxo-chelated complexes are not formed, it may be assumed that in this range two complexes, $Hg(en)_2^{2+}$ and

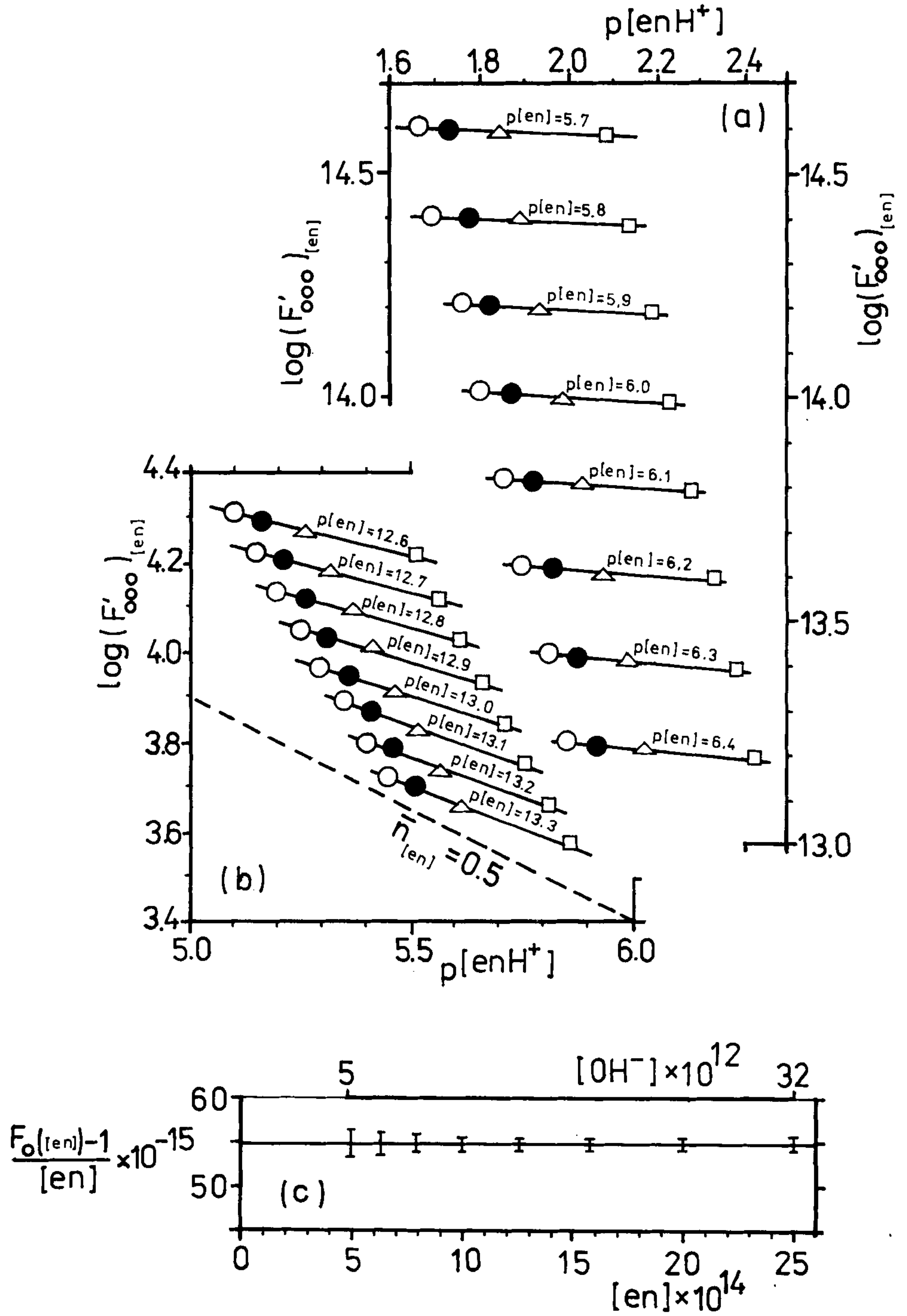

FIGURE 4 Iso-chelate functions at high (Fig. 4a) or low equilibrium 1,2-ethanediamine concentrations (Fig. 4b). For comparison the average ligand number (at constant [en]) equal to 0.5 (– – – –) is also shown; evaluation of cumulative stability constant, β_{100}, for first chelated complex (Fig. 4c).

$Hg(en)(enH)^{3+}$, do exist in labile equilibrium. The former is predominant and the contribution of the latter equals 4–9%.

On the other hand, at low values of the equilibrium chelating ligand concentration the mean $\bar{n}_{[en]}$ value changed from 0.39 to 0.26 for $p[en] = 13.3 = \text{const.}$, $p[enH^+] = 5.45 - 5.86$ and $p[en] = 12.6 = \text{const.}$, $p[enH^+] = 5.10 - 5.51$, respectively. In approximately the same ligand concentrations range $\bar{n}_{[enH^+]}$ is equal 0.61–0.83 and sum $(\bar{n}_{[enH^+]} + \bar{n}_{[en]})$ is equal to $1.0 - 1.09$. Thus, at low concentrations of en and enH^+, two complexes are predominant $(Hg(en)^{2+})$, and $Hg(enH)^{3+})$, while at $p[enH^+] = 5.2 - 5.0$ the contribution of the third complex $(Hg(en)(enH)^{3+})$ increases to about 9%. The formation of $Hg(enH)_2^{4+}$ was not observed in measurable concentrations (*c.f.* Fig. 2c). From iso-p[en] functions of complexation (*23*)

$$(F'_{000})_{[en]} = (F_0([en]))_{[en]} + \beta_1^{en}[enH^+] + \ldots \qquad (23)$$

the values of chelate complexation functions (*20*) and of the apparent stability constant (*21*) are obtained at various values of [en], by least-squares treatment. Since $(F_0([en]) - 1/[en])$, does not depend on the equilibrium concentration of chelate ligand or on the equilibrium concentration of hydroxyl ion (Fig. 4c) it may be accepted that $Hg(en)^{2+}$ is the only chelated complex over the low [en] range and that the concentration of the mixed $Hg(en)(OH)^+$ complex is negligible. Finally, the following cumulative stability constant for $Hg(en)^{2+}$ was obtained numerically: $(\beta_{100} \pm \sigma_{100}) = (5.49 \pm 0.09) \times 10^{16}$, $\log(\beta_{100} \pm \sigma_{100}) = 16.740 \pm 0.007$.

(*iii*) *Iso-pH Functions*

For $pH = 4.75 - 6.00$ (see Fig. 1) the iso-pH functions of complexation (*24*) were obtained.

$$(F'_{000})_{[H^+]} = 1 + \beta_1^{pH}[en] + \beta_2^{pH}[en]^2 \qquad (24)$$

Rearrangement leads to (*25*)

$$(G'_{200})_{[H^+]} = ((F'_{000})_{[H^+]} - 1)/[en]^2)_{[H^+]} = \beta_2^{enH} + \beta_1^{enH}([en])^{-1} \qquad (25)$$

from which the values of apparent stability constants

$$\beta_2^{pH} = \beta_{200} + \beta_{110}\, k_1^H[H^+] + \beta_{020}(k_1^H[H^+])^2 \qquad (26)$$

$$\beta_1^{PH} = \beta_{100} + \beta_{010}\, k_1^H[H^+] + \beta_{101}K_{H_2O}/[H^+] \qquad (27)$$

were determined at various $[H^+]$ values by a least-squares method (Fig. 5a–d).

The relationship between the second apparent stability constant, β_2^{pH}, and $[H^+]$ indicates that $Hg(en)_2^{2+}$ and $Hg(en)(enH)^{3+}$ are formed in significant concentrations (Fig. 5e). The lack of curvature of β_2^{pH} *vs*$[H^+]$ indicates that the contribution of the $Hg(enH)_2^{4+}$ non-chelated complex is negligible ($< 2\%$). Hence, the stability constant β_{020} could not be estimated. Finally, the following values of stability constants were evaluated numerically: $(\beta_{200} \pm \sigma_{200}) = (9.27 \pm 0.15) \times 10^{25}$, $\log(\beta_{200} \pm \sigma_{200}) = 25.967 \pm 0.007$; $(\beta_{110} \pm \sigma_{110}) = (5.65 \pm 0.25 \times 10^{20}$, $\log(\beta_{110} \pm \sigma_{110}) = 20.75 \pm 0.02$.

The rectilinear dependence of β_1^{pH} *versus* $[H^+]$, and the fact that the intercept of the straight line $(\beta_1^{pH}[H^+] = f([H^+]))$ approaches zero, indicates that $Hg(en)(OH)^+$ and $Hg(enH)^{3+}$ are not present to any significant extent under iso-pH function conditions (Fig. 6). Thus, for $pH = 4.75 - 6.00$ the first apparent stability constant (*27*) is practically equal to the cumulative stability constant for the $Hg(en)^{2+}$ chelated complex: $(\beta_{100} \pm \sigma_{100}) = (5.16 \pm 0.30) \times 10^{16}$, $\log(\beta_{100} \pm \sigma_{100}) = 16.71 \pm 0.03$.

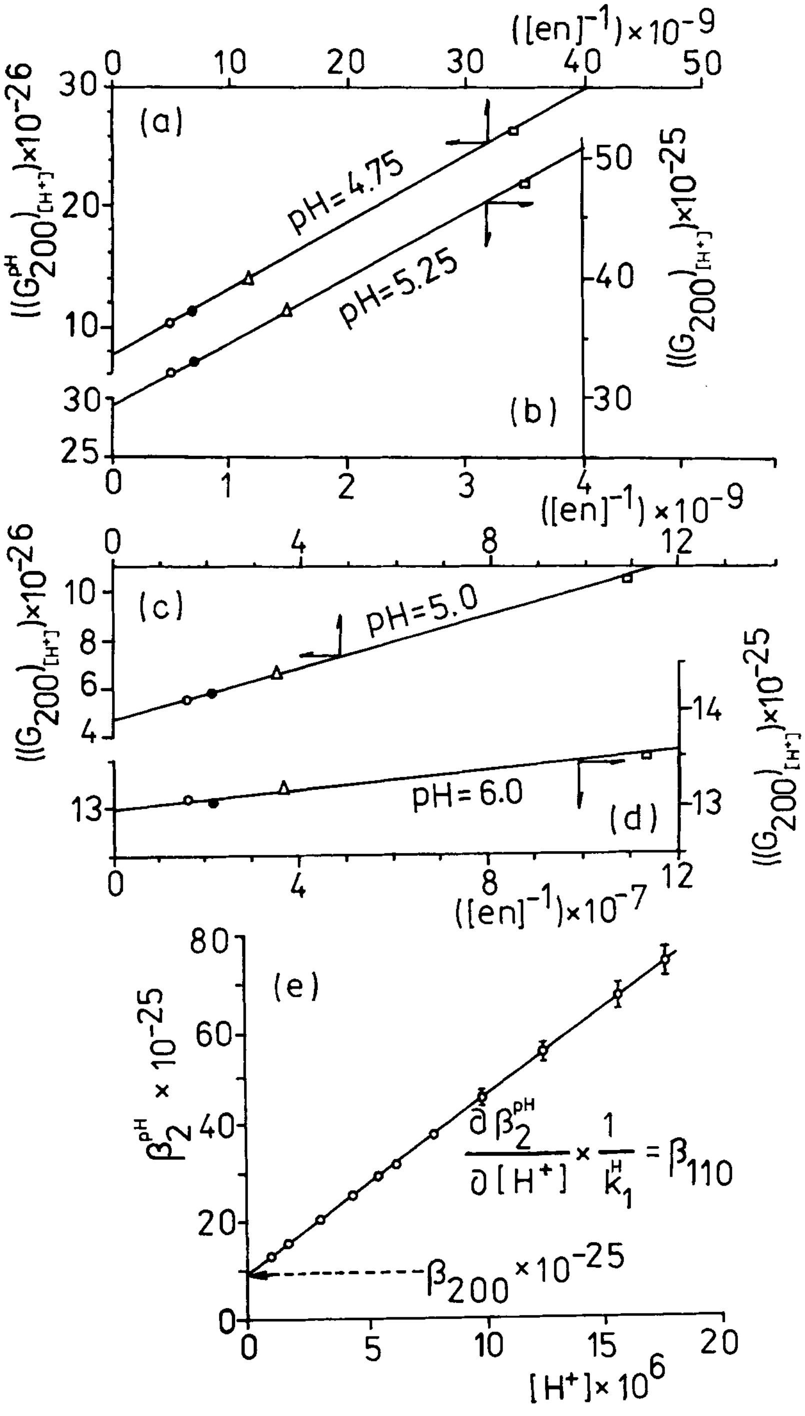

FIGURE 5 Iso-ph functions; evaluation of apparent stability constants (β_2^{pH} and β_1^{pH}) for pH = 4.75 (Fig. 5a), 5.25 (Fig. 5b), 5.00 (Fig. 5c), 6.00 (Fig. 5d); evaluation of cumulative stability constant, β_{200}, for second chelated complex and of cumulative stability constant, β_{110}^{H} or β_{110}, for partly-chelated complex (Fig. 5e).

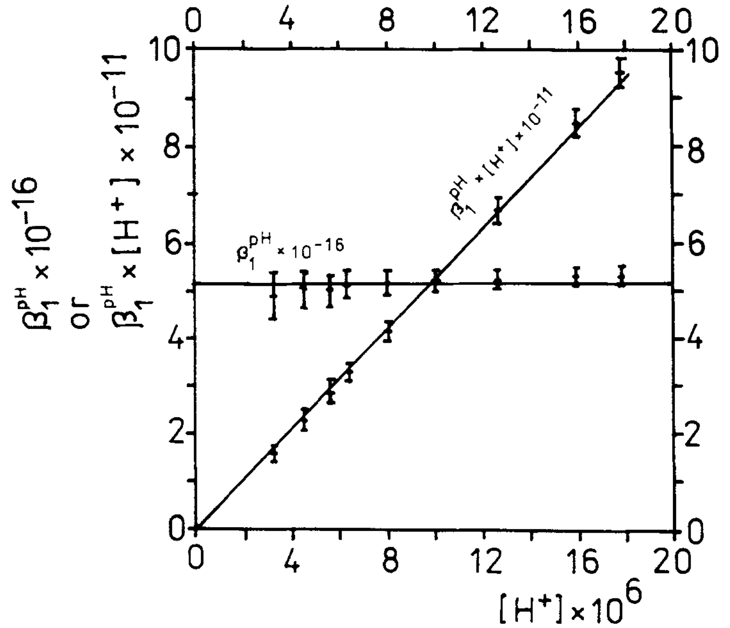

FIGURE 6 Evaluation of cumulative stability constant, β_{100}, for first chelated complex from first apparent stability constant β_1^{pH} (or $\beta_1^{pH}[H^+]$) dependence *versus* $[H^+]$.

Direct Estimation of Cumulative Stability Constants from Experimental Complexation Functions

Experimental data for the four main measurement series were the basis of the direct weighted least-squares calculations. The function minimized was

$$S = \sum_{i=1}^{i=N} w_{(F'_{000})_i} ((F'_{000})_i^{exper.} - (F'_{000})_i^{calc.})^2 \qquad (28)$$

where N is the number of experimental points and $w_{(F'_{000})_i} = 1/(F'_{000})_i^2$ is the relative weight of the i-th data point. A representative part of the data is listed in Table II. During the verification of different equilibrium models, no complexes containing more than one 2-aminoethylammonium cation or mixed (hydroxo-chelated) complexes were found to be formed. The final results of the computer calculations are summarized in Table III. A comparison between those obtained from iso-concentration functions and directly evaluated values of cumulative stability constants from experimental complexation functions shows good agreement.

The distribution of Hg(II) among various complexes is shown in Fig. 7. For $pH \geqslant 4.75$ $Hg(enH)^{3+}$ can be neglected; on the other hand, for $3 < pH < 4.5$, the concentration of the $Hg(en)_2^{2+}$ complex may be neglected at all $C_{enH_2(ClO_4)_2}$ under investigation. A good agreement between the stability constants determined over the pH range from 3 to 7 and those obtained for both above ranges† indicates that our assumption neglecting Hg_2^{2+} compexation with en or enH^+ is justified.[22]

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†For instance, $C_{enH_2(ClO_4)_2} = 0.15$ M and $4.953 \leqslant pH \leqslant 6.839$, the following values: $\log \beta_{100} = 16.756 \pm 0.072$, $\log \beta_{110} = 20.753 \pm 0.030$, $\log \beta_{200} = 25.970 \pm 0.009$, and for $3.093 \leqslant pH \leqslant 4.385$ very close values: $\log \beta_{010} = 8.803 \pm 0.054$, $\log \beta_{100} = 16.756 \pm 0.021$, $\log \beta_{110} = 20.737 \pm 0.078$ were obtained, respectively.

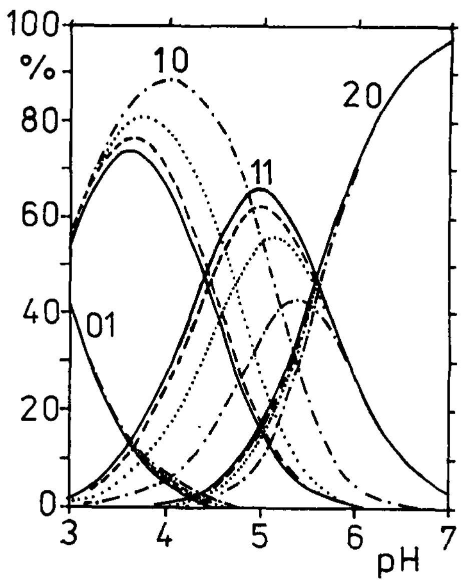

FIGURE 7 Distribution of Hg(II) among various complexes as a function of pH for the series with $C_{enH_2(ClO_4)_2} = 0.3333$ M (-----), 0.25 M (– – –), 0.15 M (····), 0.05 M (-·-·-·-); 10 = $Hg(en)^{2+}$, 01 = $Hg(enH)^{3+}$, 11 = $Hg(en)(enH)^{3+}$, 20 = $Hg(en)_2^{2+}$. The curves are calculated with $\beta_{10} = 10^{16.749}$, $\beta_{01} = 10^{8.821}$, $\beta_{01} = 10^{20.751}$, $\beta_{20} = 10^{25.970}$.

Comparison of the results obtained here with those of Bjerrum and Larsen[2] reveals one basic difference; no formation of $Hg(enH)_2^{4+}$ is observed, but the existence of the mixed $Hg(en)(enH)^{3+}$ complex is demonstrated (Table I). Under these circumstances we have repeated calculations for the data provided by Bjerrum and Larsen (Table 4 in Ref. 2) using our computer program for calculation of stability constants.[30] For the Bjerrum and Larsen set of linear equations $(X - \beta_{20}[en]^2)$‡ the best solution was achieved for the Bjerrum and Larsen original model: $\log(\beta_{10} \pm \sigma_{10}) = 14.343 \pm 0.068$, $\log(\beta_{02} \pm \sigma_{02}) = 14.125 \pm 0.068$, SSR = 5.50×10^{-2}, $\delta_{E_{Hg}} = 3.01$ mV (*c.f.* Table I of this work). However, for the same function an acceptable solution (somewhat higher SSR and acceptable δ_{ij}) was obtained with the assumption that, instead of $Hg(enH)_2^{4+}$, the mixed $Hg(en)(enH)^{3+}$ complex is formed: $\log(\beta_{10} \pm \sigma_{10}) = 14.203 \pm 0.134$, $\log(\beta_{11} \pm \sigma_{11}) = 18.595 \pm 0.088$, SSR = 8.54×10^{-2}, $\delta_{E_{Hg}} = 3.75$ mV. The differences between both models diminished, when for the same data (Table 4 in Ref. 2) the calculations were performed directly from the function $X = C_{Hg^{2+}}/[Hg^{2+}]$. In that case, for the model comprising $Hg(en)^{2+}$, $Hg(enH)_2^{4+}$, $Hg(en)_2^{2+}$, the following values were obtained: $\log(\beta_{10} \pm \sigma_{10}) = 14.313 \pm 0.136$, $\log(\beta_{02} \pm \sigma_{02}) = 14.064 \pm 0.074$, $\log(\beta_{20} \pm \delta_{20}) = 23.463 \pm 0.041$, SSR = 6.88×10^{-2}, $\delta_{E_{Hg}} = 1.07$ mV, while for the model comprising $Hg(en)^{2+}$, $Hg(en)(enH)^{3+}$, $Hg(en)_2^{2+}$): $\log(\beta_{10}) = 14.299 \pm 0.142$, $\log(\beta_{11} \pm \sigma_{11}) = 18.826 \pm 0.075$, $\log(\beta_{20} \pm \sigma_{20}) = 23.353 \pm 0.069$, SSR = 7.04×10^{-2}, $\delta_{E_{Hg}} = 1.08$ mV. Thus, both models are statistically equivalent (F-test). From the theory of reversible step reactions[3] it follows that formation of $Hg(en)_2^{2+}$ and $Hg(enH)_2^{4+}$ should be accompanied by the presence of the $Hg(en)(enH)^{3+}$ complex, acording to

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‡β_{20} was found by independent measurement.[2]

TABLE II

Results of glass- and Hg-electrode measurement in 3M (Na,H)ClO$_4$ = 9.5057 × 10^{-4} M, $C_{enH_2(ClO_4)_2}$ = 0.15 M, $C_{NaClO_4} = 3 - 2C_{enH_2(ClO_4)_2} - 2C_{Hg(ClO_4)_2}$ · $pk_1^H = 10.81$, $pk_{12}^H = 7.93$ (Ref. 9).

No.	pH	p[Hg^{2+}]	p[en]	p[enH$^+$]	logF$'_{000}$	No.	pH	p[Hg^{2+}]	p[en]	p[enH$^+$]	log F$'_{000}$
1	6.839	17.177	5.915	1.944	14.1555	17	4.851	10.309	9.858	3.899	7.2867
2	6.781	16.957	6.029	1.998	13.9354	18	4.737	10.005	10.086	4.013	6.9828
3	6.705	16.673	6.175	2.070	13.6510	19	4.624	9.720	10.312	4.126	6.6979
4	6.610	16.316	6.360	2.160	13.2942	20	4.500	9.422	10.560	4.250	6.3996
5	6.490	15.863	6.595	2.275	12.8408	21	4.385	9.151	10.790	4.365	6.1293
6	6.375	15.420	6.822	2.387	12.3984	22	4.242	8.827	11.076	4.508	5.8052
7	6.219	14.828	7.130	2.539	11.8062	23	4.088	8.493	11.384	4.662	5.4703
8	6.063	14.241	7.440	2.693	11.2192	24	3.917	8.137	11.726	4.833	5.1139
9	5.922	13.731	7.720	2.832	10.7088	25	3.751	7.806	12.058	4.999	4.7810
10	5.739	13.081	8.085	3.014	10.0588	26	3.591	7.508	12.379	5.160	4.4796
11	5.619	12.660	8.324	3.133	9.6384	27	3.456	7.263	12.649	5.295	4.2301
12	5.478	12.178	8.605	3.273	9.1563	28	3.342	7.057	12.877	5.409	4.0174
13	5.308	11.649	8.945	3.443	8.6269	29	3.239	6.881	13.083	5.512	3.8323
14	5.151	11.157	9.260	3.600	8.1350	30	3.154	6.747	13.253	5.597	3.6875
15	5.059	10.895	9.443	3.692	7.8730	31	3.093	6.650	13.375	5.658	3.5813
16	4.953	10.596	9.654	3.798	7.5738						

TABLE III

Results of computer calculations of stability constants for 143 experimental points with $C_{enH_2(ClO_4)_2} = 0.3333$ M (39 points), 0.25 M (35 points, 0.15 M (31 points, 0.05 M (38 points); $C_{Hg(ClO_4)_2} = 9.5057 \times 10^{-4}$ M, $C_{NaClO_4} = 3 - 2C_{enH_2(ClO_4)_2} - 2C_{Hg(ClO_4)_2}$.

Equilibrium	$\beta_{ij} \pm 3\sigma\beta_{ij}$
$Hg^{2+} + enH^{+} \rightleftharpoons Hg(enH)^{3+}$	$(66.19 \pm 2.83) \times 10^{7}$
$Hg^{2+} + en \rightleftharpoons Hg(en)^{2+}$	$(56.16 \pm 0.78) \times 10^{15}$
$Hg^{2+} + en + enH^{+} \rightleftharpoons Hg(en)(enH)^{3+}$	$(56.41 \pm 0.87) \times 10^{19}$
$Hg^{2+} + 2\,en \rightleftharpoons Hg(en)_2^{2+}$	$(93.23 \pm 0.71) \times 10^{24}$

$SSR = 10^{-4}$, $\sigma_{E_{Hg}} = 0.19$ mV.

the reaction $Hg(en)_2^{2+} + Hg(enH)_2^{4+} \rightleftharpoons 2Hg(en)(enH)^{3+}$. On the other hand, the results of the model[21] and experimental studies of zinc family cations — ethanediamine complexation obviously indicate[9,11] that the contribution of the $M(en)(enH)^{3+}$ mixed complex increases strikingly with increase of the total ligand salt concentration (Fig. 7). Comparison of the total concentration ranges ($C_{enH_2(ClO_4)_2} = 0.33 - 0.05$ M, this work, $C_{enH_2^{2+}} = 0.05 - 4 \times 10^{-4}$ M, Ref. 2) shows that under our chosen conditions the formation of $Hg(en)(enH)^{3+}$ is preferred. It is also remarkable that Hg(II) — ethanediamine complexes change in configuration from planar ($Hg(en)^{2+}$) to tetrahedral ($Hg(en)_2^{2+}$, Ref. 31). This fact could be easily explained by the assumption that the configuration proceeds through the $Hg(en)(enH)^{3+}$ mixed complex cation. It could be concluded therefore, that the final values of the cumulative stability constants (last column of Table III) are a good approximation for calculations of the equilibrium concentrations of $Hg(en)_i(enH)_j$ complexes coexisting in labile equilibrium in 3 M $(Na,H)ClO_4$.

SUPPLEMENTARY MATERIAL

A listing of data (F'_{000}) for all experimental points and results are available upon request from the Editor.

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