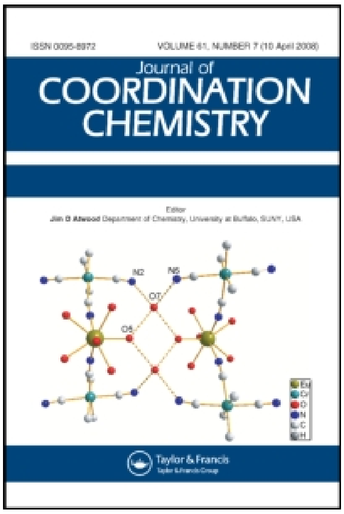

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REFINEMENT OF COMPLEXATION EQUILIBRIA MODELS FOR THE MERCURY(II)-ETHANEDIAMINE SYSTEM

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REFINEMENT OF COMPLEXATION EQUILIBRIA MODELS FOR THE MERCURY(II)-ETHANEDIAMINE SYSTEM

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The three existing models for mercury(II)–ethanediamine equilibria are in considerable disagreement. It has been demonstrated that all three sets of experimental data (obtained by different authors) can be best explained on the basis of the same model of complexation: $Hg(en)_2^{2+}$, $Hg(en)(enH)^{3+}$, $Hg(en)^{2+}$, $Hg(enH)^{3+}$, while the formation of the latter complex for $pH > 4$ may be neglected. Refined stability constants for chelated and protonated mercury(II)–ethanediamine complexes are presented.

Keywords: Mercury(II), 1,2-diaminoethane, stability constants, refinement, speciation

INTRODUCTION

Watters and Mason[1] reported the formation of the complexes $Hg(en)_2^{2+}$, $Hg(en)^{2+}$, $Hg(en)(OH)^+$, $Hg(en)(enH)^{3+}$, $Hg(enH)_2^{4+}$ and $Hg(en)(enH)_2^{4+}$ in the mercury(II)–ethanediamine—0.1 M $NaClO_4$ system at 25°C (en and enH^+ represent 1,2-ethanediamine and 2-aminoethylammonium cation, respectively). This model of the complexation equilibria[1] is surprisingly different to that of Bjerrum and Larsen model[2] ($Hg(en)_2^{2+}$, $Hg(en)^{2+}$, $Hg(enH)_2^{4+}$, $Hg(enH)^{3+}$) in 1.3 M KNO_3 at 25°C, and also to our model[3] ($Hg(en)_2^{2+}$, $Hg(en)(enH)^{3+}$, $Hg(en)^{2+}$, $Hg(enH)^{3+}$) in 3 M $NaClO_4$ at 25°C. It should be mentioned that all three models[1-3] are based upon potentiometric measurements of concentrations (non-complexed Hg(II) and ligands) using the mercury and glass electrode, respectively. Under these circumstances, a critical analysis of the models of the complexation equilibria for the above mentioned system would seem to be reasonable (*c.f.*, Ref. 4, p. 519).

EXPERIMENTAL

To clarify the observed discrepancies between the existing equilibrium models for the Hg(II)-en system, the Watters and Mason data were reproduced[5] and direct weighted least-squares calculations of the overall stability constants were performed, assuming different equilibrium models. The function minimized was

$$SSR = \sum_{i=1}^{i=N} {}^{w}(F_{ooo})_i \left((F^{exp}_{ooo})_i - (F^{calc}_{ooo})_i\right)^2$$

where N is the number of experimental points,

$${}^{w}(F_{ooo})_i = 1/(F_{ooo})_i^2$$

is the relative weight of the i-th data point,

$$F_{ooo} = \sum_{i=O}^{i=N} \sum_{j=O}^{j=M} \sum_{k=O}^{k=K} \beta_{ijk}[en]^i[enH^+]^j[OH^-]^k$$

is the total complexation function, and

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

is the overall stability constant.

RESULTS AND DISCUSSION

The results of the computer verification of the different equilibrium models are summarized in Table I. Comparison of the stability constants obtained by Watters and Mason (model I) with those estimated in this paper (model II) showed satisfactory agreement. It could thus be assumed that the present calculations (limited to two from among four measuring series)[5] are a satisfactory representation of the whole of the Watters and Mason data.[1]. Therefore the models II–V (Table I) could be compared with each other and with models reported by other authors[2-3] (Table II). For that purpose, in Tables I and II are listed also the values of the sum of the weighted squares of residuals, SSR, and the estimated error in the mercury electrode measurements, $\sigma_{E_{Hg}}$.[6] Assuming the liberal criterion for retaining any particular complex within a given model,[7] $\sigma_{\log\ \beta_{ijk}} \leqslant 0.15$, we discover that the standard deviation is less than or equal to 0.15 for log β_{200} only in models II–IV, and for log β_{200} and log β_{100} in model V. However, even for the most plausible model, V, the standard deviation for the mixed $Hg(en)(enH)^{3+}$ complex still exceeds the above criterion and is equal to 0.167 (*c.f.*, in the original Watters and Mason model[1] it is six times lower). In fact, the SSR and $\sigma_{E_{Hg}}$ values for models 1–V are very high and this points towards a rather poor total precision for the above data. For this reason the SSR value declines somewhat with a simultaneous and considerable increase of the $\sigma_{\log\ \beta_{ijk}}$ value for model II towards V. Thus, none of the models summarized in Table I can be chosen following statistical criteria (including F-test). In this situation the model choice should be based upon considerations[8] of model simplicity, model similarity and the chemical significance of the selected complexes. For that purpose in Table II are gathered the models obtained for the Watters and Mason data (V), Bjerrum and Larsen[2] (VI, see also Ref. 3), and for our data[3] (VII). The following points could be concluded concerning the models listed in Table II. They are as simple as possible; two latter do not contain the poorly defined complexes. They are consistent with each other including the fact the latter model comprises data at pH $\geqslant 3$ and hence the presence of the $Hg(enH)^{3+}$ non-chelated complex. In addition, chemical significance of the selected complexes could be visualized by the pathway $Hg^{2+} \rightarrow Hg(enH)^{3+} \rightarrow Hg(en)^{2+} \rightarrow Hg(en)(enH)^{3+} \rightarrow Hg(en)_2^{2+}$. The above scheme also provides the course of configuration equilibria from linear $Hg(enH)^{3+}$ or planar $Hg(en)^{2+}$ to tetrahedral $Hg(en)_2^{2+}$ *via* the Hg(en) $(enH)^{3+}$ mixed complex.[3] It is noteworthy that analogous complexes are formed with the other zinc family cations where the mixed $M(en)_2(enH)^{3+}$ complex contribute to the tetrahedron–octahedron configuration equilibrium.[9-11]

TABLE I

Results of computer calculations of stability constants for the $Hg(en)_i(enH)_j(OH)_k^{(2+j-k)+}$ complexes for the Watters and Mason data.[1,5]

$\log \beta_{ijk} \pm \sigma \log \beta_{ijk}$	I[a]	II[b]	III[b]	IV[b]	V[b]
$\log \beta_{200} \pm \sigma \log \beta_{200}$	23.3 ± 0.1	23.341 ± 0.087	23.439 ± 0.105	23.403 ± 0.086	23.403 ± 0.077
$\log \beta_{100} \pm \sigma \log \beta_{100}$	14.3 ± 0.1	14.179 ± 0.374	14.534 ± 0.230	14.458 ± 0.262	14.458 ± 0.150
$\log \beta_{010} \pm \sigma \log \beta_{010}$				5.291 ± 288.9	
$\log \beta_{101} \pm \sigma \log \beta_{101}$	23.8 ± 0.3	23.865 ± 0.214			
$\log \beta_{110} \pm \sigma \log \beta_{110}$	18.6 ± 1.0	18.459 ± 1.229		19.169 ± 0.188	19.169 ± 0.167
$\log \beta_{120} \pm \sigma \log \beta_{120}$	22.3 ± 0.3	21.994 ± 0.340			
$\log \beta_{020} \pm \sigma \log \beta_{020}$	12.9 ± 0.1	13.012 ± 0.377	12.747 ± 1.003		
SSR		0.0857	0.2518	0.1390	0.1111
$\sigma_{E_{Hg}}$ (mV)		3.76	6.45	4.79	4.28

[a] Watters and Mason original results (*c.f.*, Table II in Ref. 1); [b] Results for Watters and Mason data reproduced in this work.[5]

TABLE II

Comparison of the results of computer calculations of stability constants for the $Hg(en)_i(enH)_j^{(2+j)+}$ complexes: model V: Watters and Mason data,[5] model VI: Bjerrum and Larsen data (*c.f.*, Refs. 2 and 3), model VII: present author's data (Ref. 3).

$\log \beta_{ijk} \pm \sigma \log \beta_{ijk}$	V[a]	VI[b]	VII[c]
$\log \beta_{200} \pm \sigma \log \beta_{200}$	23.403 ± 0.077	23.353 ± 0.069	25.970 ± 0.003
$\log \beta_{100} \pm \sigma \log \beta_{100}$	14.458 ± 0.150	14.299 ± 0.142	16.749 ± 0.006
$\log \beta_{110} \pm \sigma \log \beta_{110}$	19.169 ± 0.167	18.826 ± 0.075	20.751 ± 0.007
$\log \beta_{010} \pm \sigma \log \beta_{010}$			8.82 ± 0.02
SSR	0.1111	0.0704	2.15×10^{-4}
$\sigma_{E_{Hg}}$ (mV)	4.28	1.08	0.19
Medium	0.1 M $NaClO_4$	1.3 M KNO_3	3 M $NaClO_4$

[a] $C_{Hg(ClO_4)_2} = 0.001$–0.01 M, $C_{en} = 0.005$–0.07084 M; [b] $C_{Hg(NO_3)_2} = 3.64 \times 10^{-5}$–$0.002$ M, $C_{en} = 3.71 \times 10^{-4}$–$0.0525$ M; [c] $C_{Hg(ClO_4)_2} = 1.90 \times 10^{-4}$–$9.51 \times 10^{-4}$ M, $C_{enH_2(ClO_4)_2} = 0.05$–$0.3333$ M.

It could be concluded therefore, that the models V–VII should be regarded as the best justified solutions for the data reported by Watters and Mason[1] (V), Bjerrum and Larsen[2] (VI), and for our data[3] (VII), respectively. Moreover, all three data sets[1-3] could ultimately be explained on the basis of the same model of complexation, $Hg(en)_2^{2+}$, $Hg(en)(enH)^{3+}$, $Hg(en)^{2+}$, $Hg(enH)^{3+}$, without regard to the formation of the latter complex for pH > 4 (Figure 1).

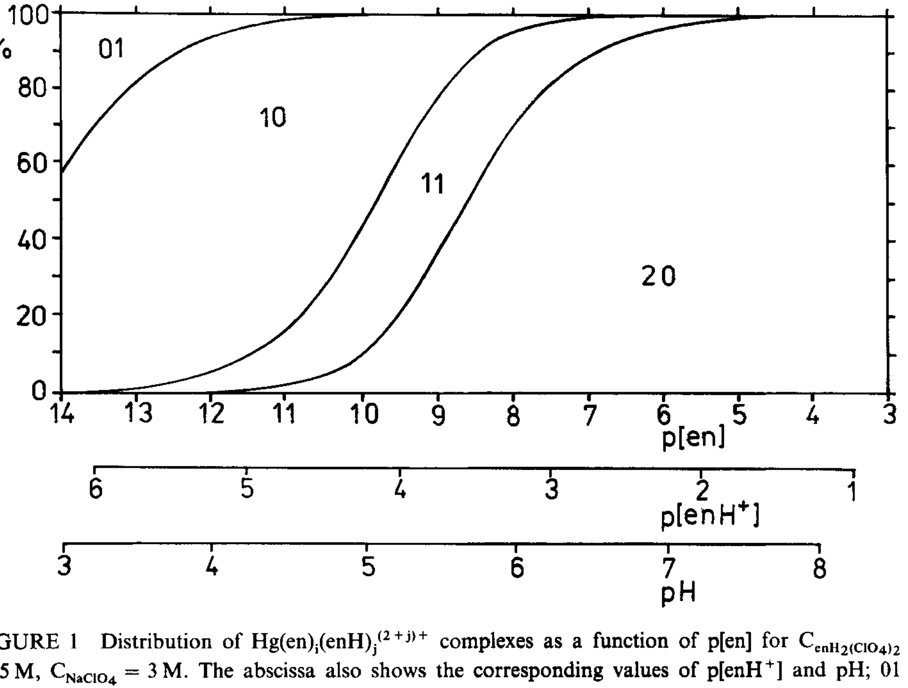

FIGURE 1 Distribution of $Hg(en)_i(enH)_j^{(2+j)+}$ complexes as a function of p[en] for $C_{enH_2(ClO_4)_2} = 0.05$ M, $C_{NaClO_4} = 3$ M. The abscissa also shows the corresponding values of p[enH⁺] and pH; 01 = $Hg(enH)^{3+}$, 10 = $Hg(en)^{2+}$, 11 = $Hg(en)(enH)^{3+}$, 20 = $Hg(en)_2^{2+}$, calculated with $\beta_{01} = 10^{8.82}$, $\beta_{10} = 10^{16.749}$, $\beta_{11} = 10^{20.751}$, $\beta_{20} = 10^{25.970}$.

SUPPLEMENTARY MATERIAL

A one page listing of data (F_{000} = f([en],[enH$^+$],[H$^+$]) is available upon request from the Editor.

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6. Watters and Mason do not report the experimental data E_{Hg} and for that reason only the relative $\sigma_{E_{Hg}}$ values could have been estimated according to the relation: $\sigma_{E_{Hg}} = ((\partial_{E_{Hg}}/\partial[Hg^{2+}])/2.303)\, SSR^{1/2}$, using $\partial_{E_{Hg}}/\partial[Hg^{2+}] = 29.58$ mV.
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